



Electrochemical characterization and performance evaluation

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Electrochemical characterization and performance evaluation



Mogens Mogensen

Fuel Cells and Solid State Chemistry

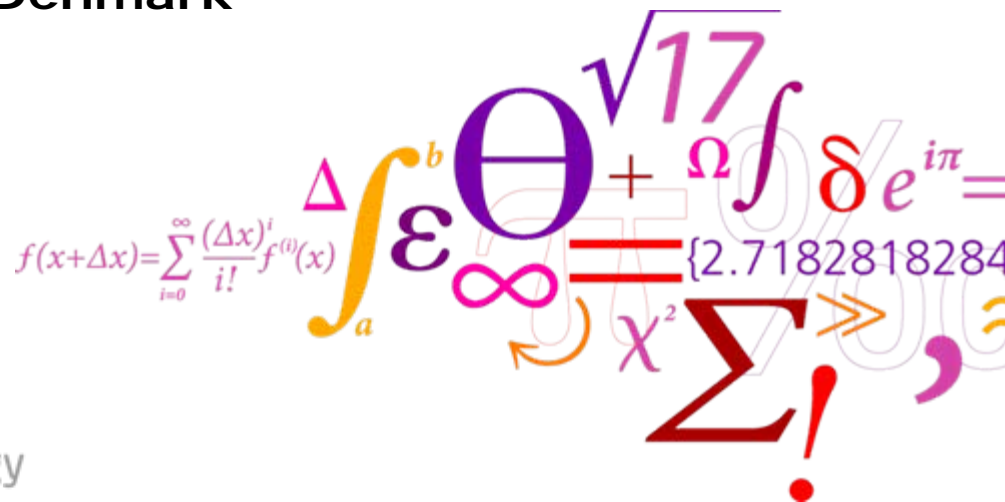
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Risø DTU

National Laboratory for Sustainable Energy

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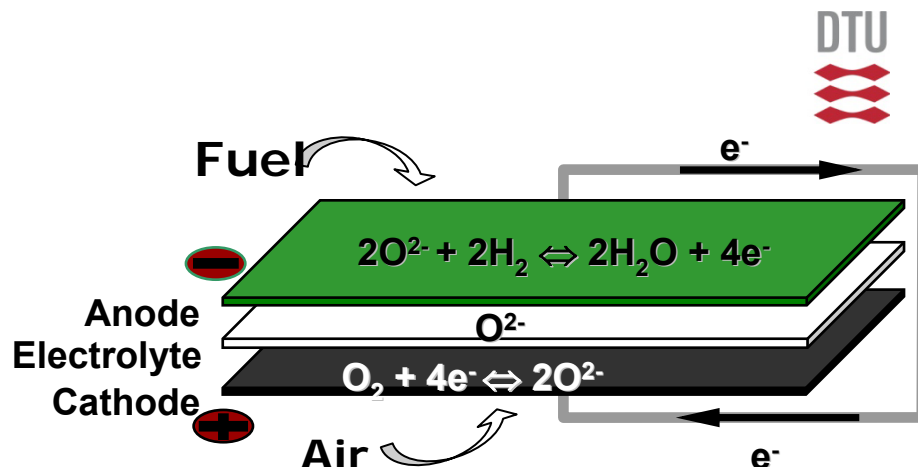
Introduction

Objective of electrochemical characterization:

- Gain further insight on the behaviour of each individual cell component
- Assist production
- Enable further development and performance optimisation

Main goal is:

- Increase knowledge
- Increase energy efficiency
- Knowledge to \$\$\$\$



- Electrolyte resistance
- Contact resistance on all interfaces
- Polarization resistance (electrodes)
- Gas diffusion limitations
- Gas conversion
- Leakage of all kinds

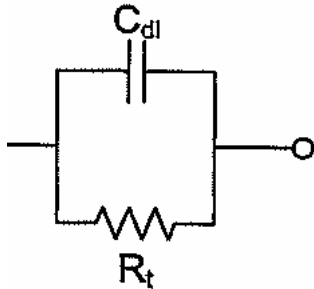
All contributing to the losses

Electrochemical Impedance Spectroscopy, EIS

- EIS is very strong tool in the process of break down the total electrode impedance into the contributions from the various components of the cell.
- EIS does not replace i - V curves (current density vs. cell voltage)
- It is most often wise and often necessary to supplement (enhance) the electrical characterisation of the cell with microscopic or surface analysis examination methods

IS of electrical RC parallel circuit

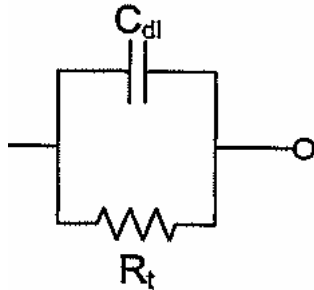
- The simplest equivalent circuit (model) of an electrode is a parallel connection between a capacitor and a resistor:



- The total current is the sum of two currents

$$i = i_C + i_F$$

- The Total impedance, $Z_{total} = 1/(1/Z_R + 1/Z_C)$
- Z_C is infinite for DC, i.e. no current goes through
- Z_C is 0 for infinite high frequencies

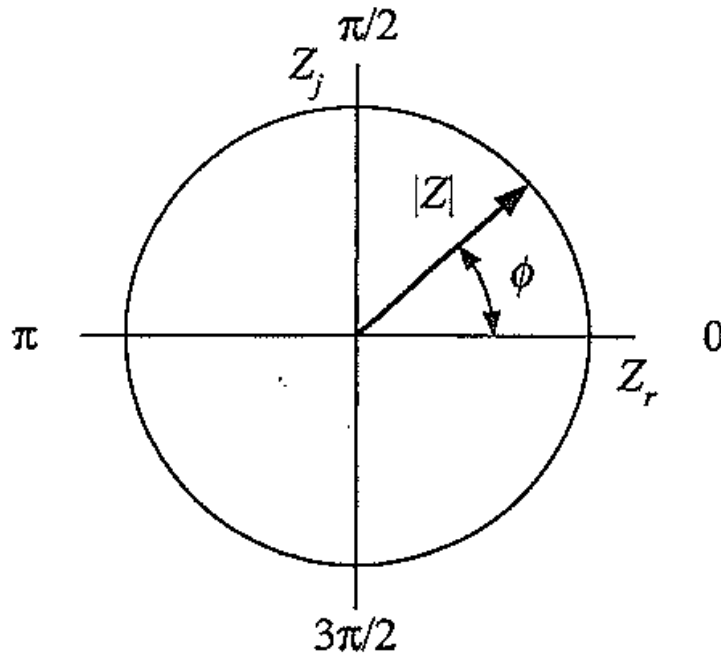


$$i_C = C \frac{d(\pi - \phi)}{dt} = C \frac{d\eta}{dt}$$

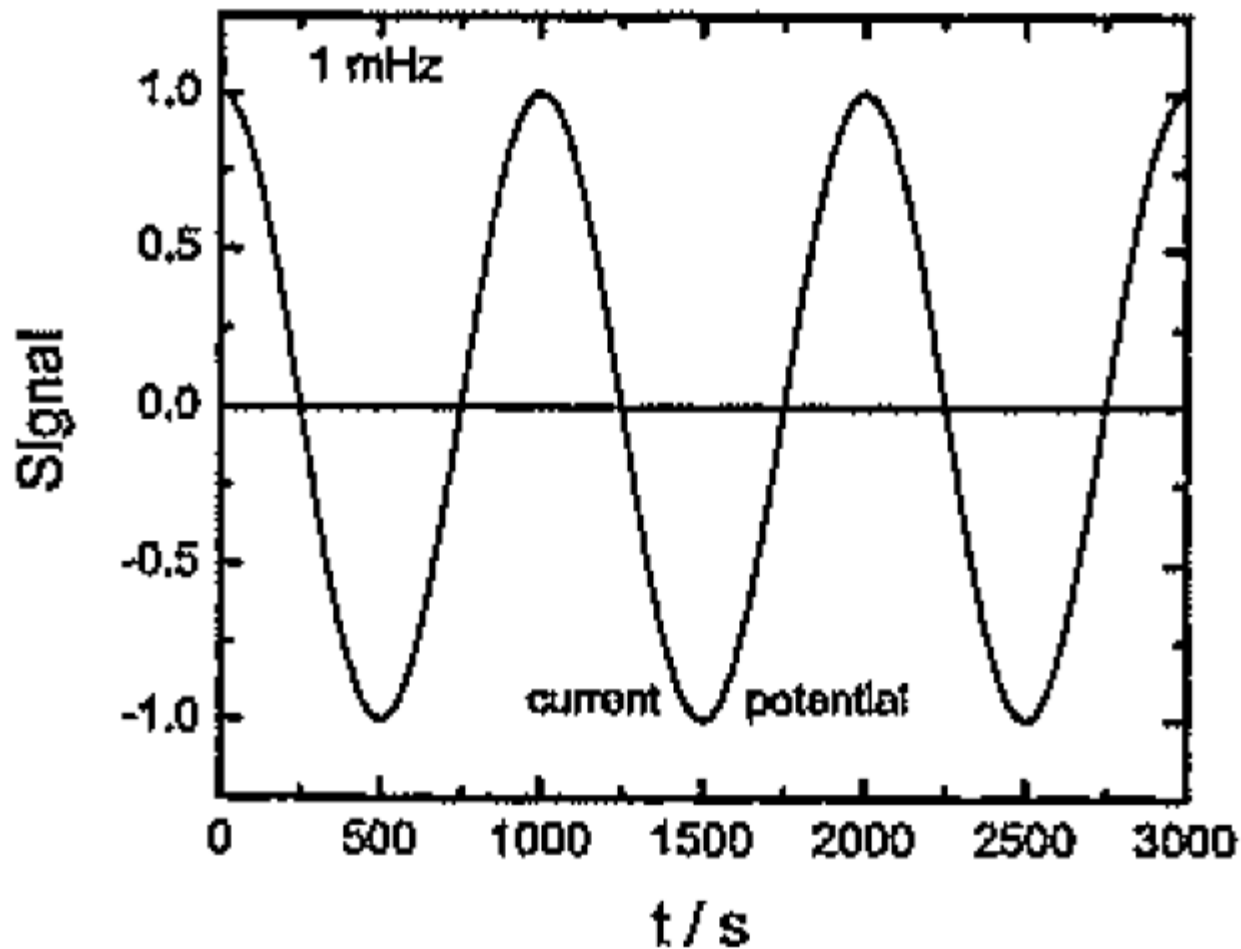
Sinusoidal voltage applied onto this.

Angular frequency $\omega = 2\pi f$ (rad/s)

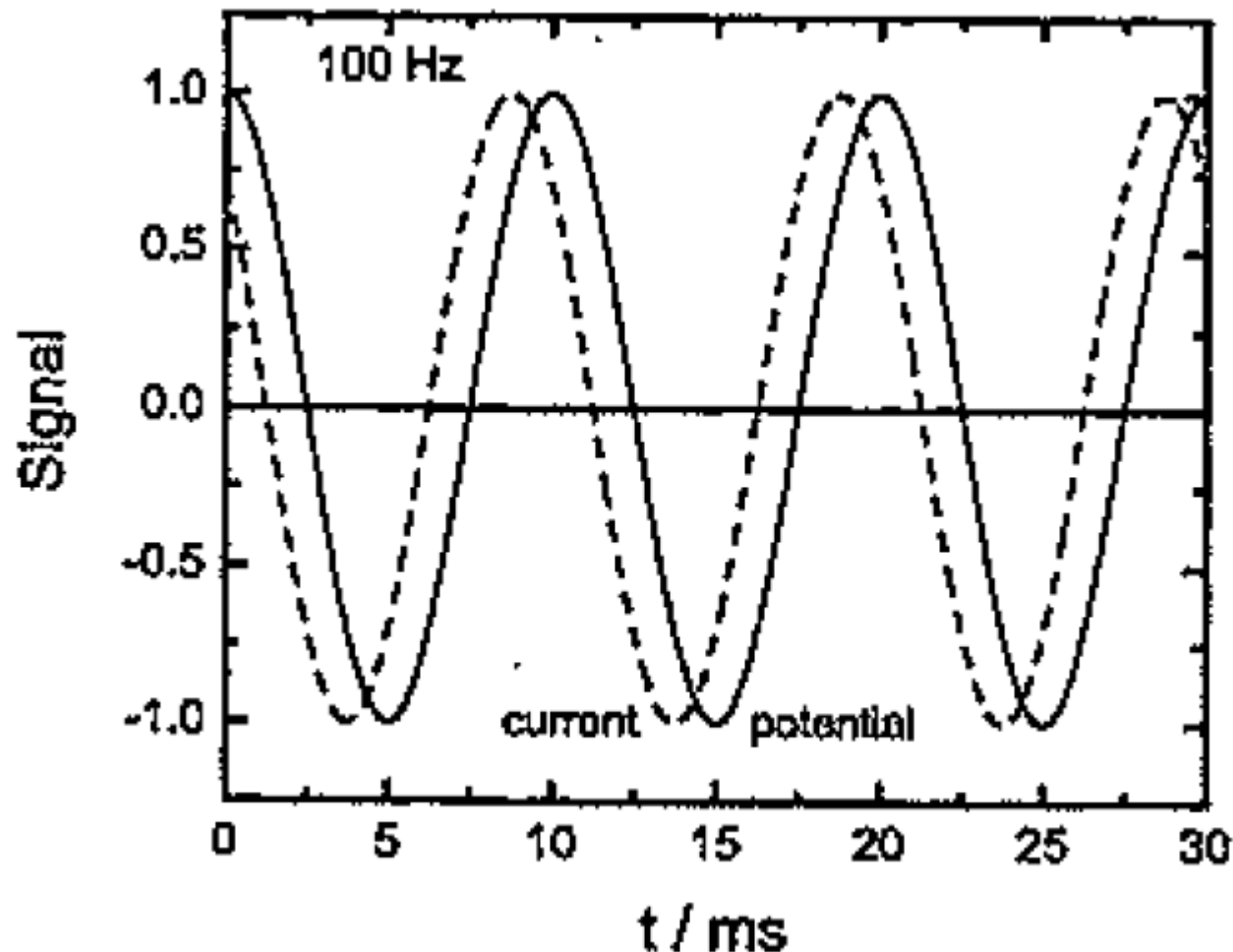
ϕ is the phase shift of the voltage relative to the current. For a capacitor the voltage is always "behind" the current, and ϕ is *negative*



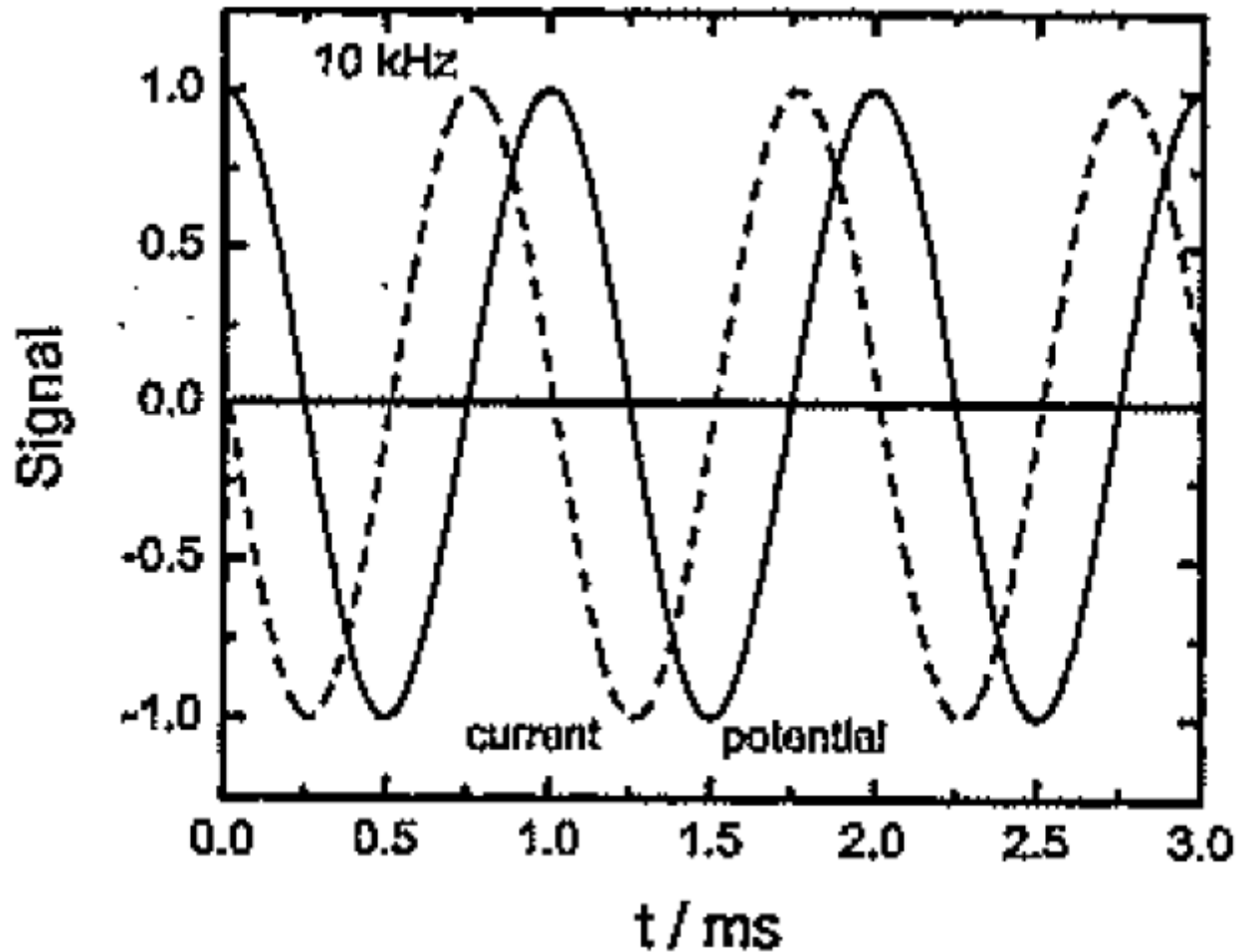
Very low frequency - phase angle is 0 - resistor



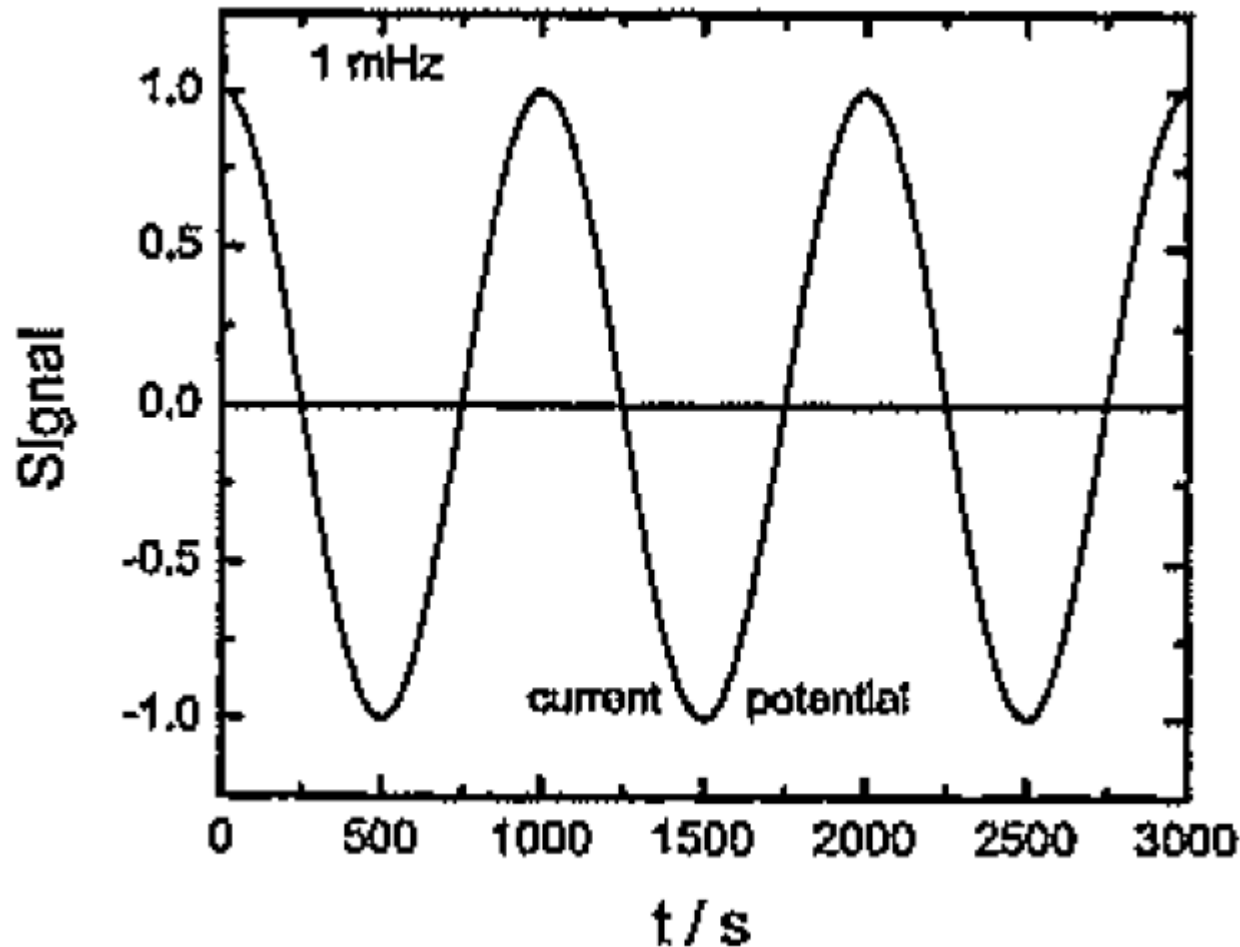
Higher frequency - phase shift < 0 for capacitance containing circuit



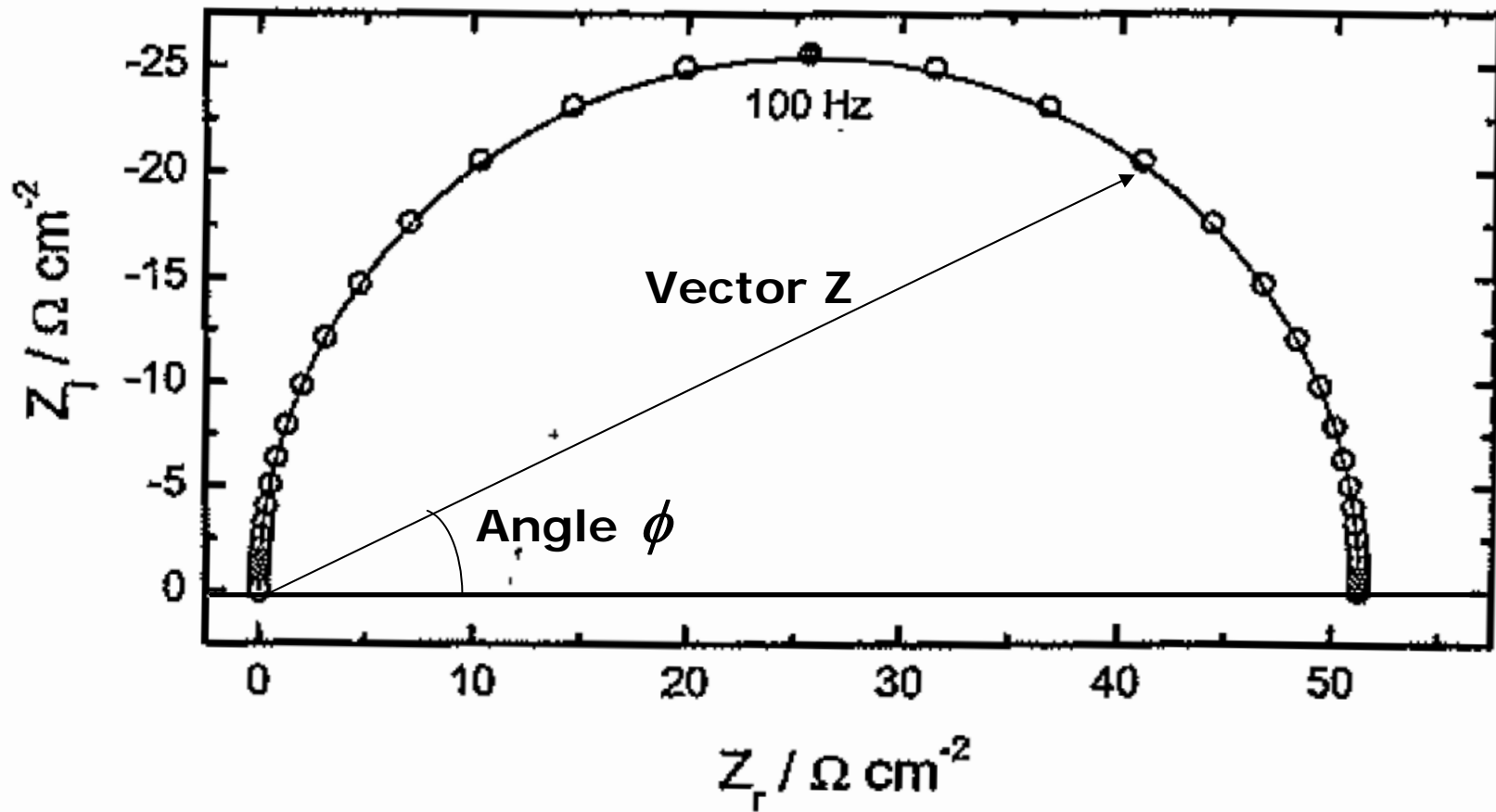
Still higher frequency



Very high frequency - phase angle is 0 again - capacitor

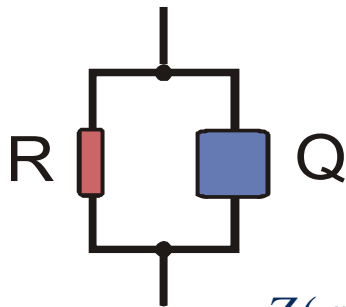


An impedance is a complex number

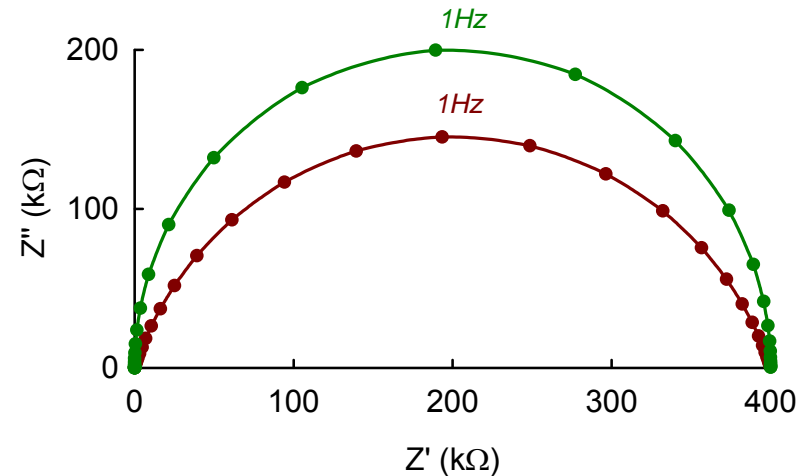


Equivalent circuits

An equivalent circuit can consist of several, combined elements, like resistors, capacitors, inductors and constant phase elements (CPEs)



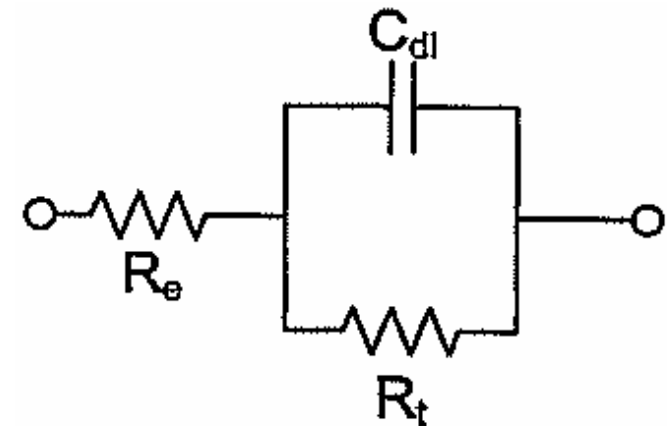
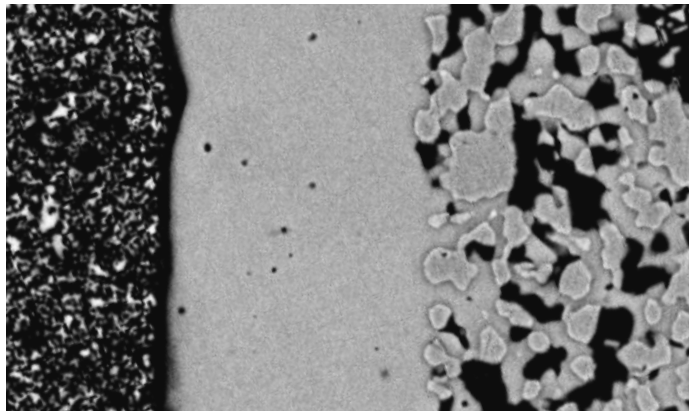
$$Z(\omega) = \left(R^{-1} + Q \cdot (i\omega)^n \right)^{-1}$$



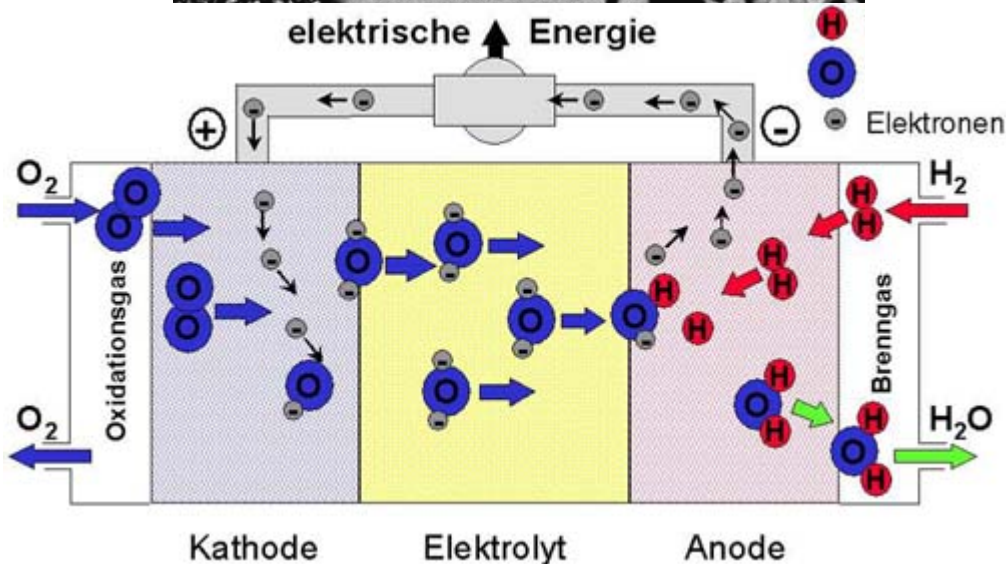
An equivalent circuit can be developed to describe the system and separate the magnitude of the physical processes:

- Several impedance spectra are required, recorded at e.g. different temperatures and gas compositions

Equivalent circuits and the cell

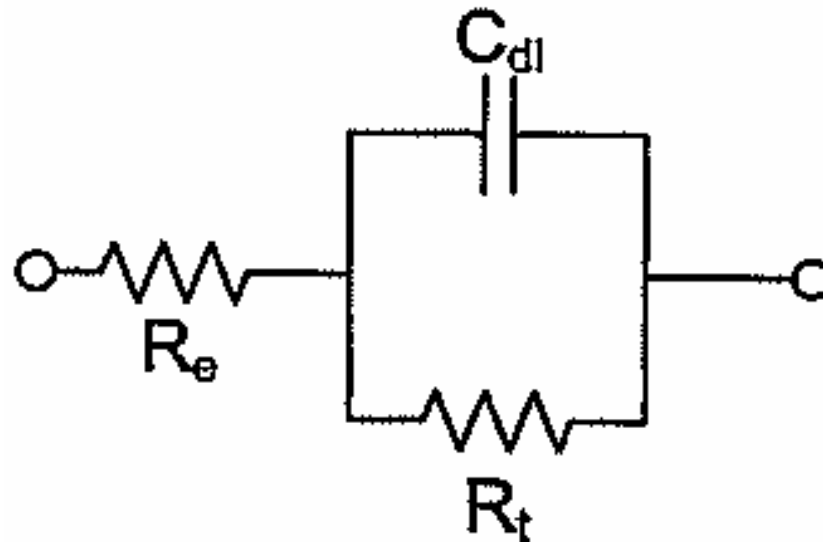


Unfortunately, the EIS of a solid oxide cell is much more complicated than the spectrum of the equivalent circuit above



Electrical Circuits

-Series and Parallel Connections

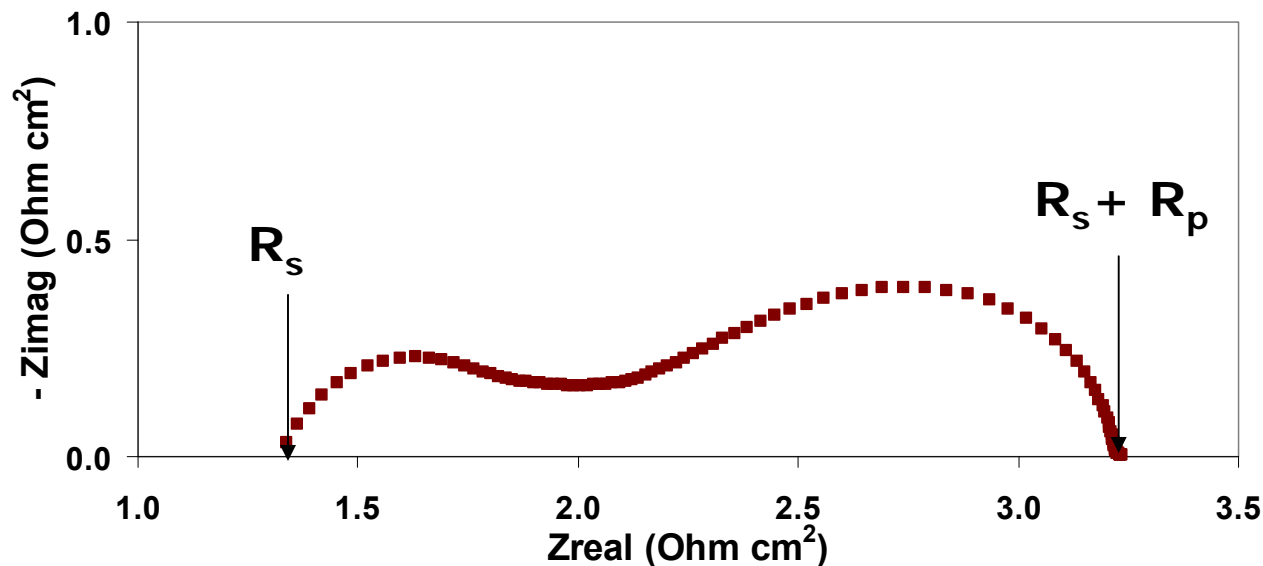


$$Z = R_e + \frac{R_t}{1 + j\omega R_t C_{dl}}$$

Graphical representations of EIS spectra

Different, complementary information can be obtained by plotting the data in different forms, for example:

Nyquist plot

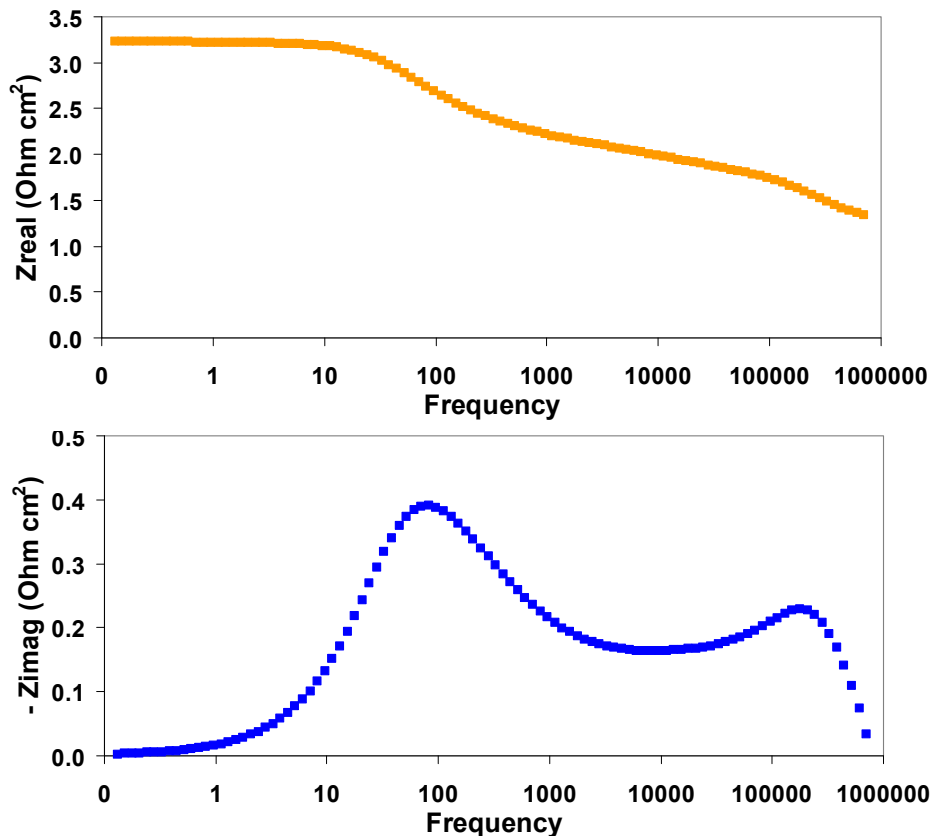


Orazem et al. 2006, J. Electrochem. Soc. 153 B129

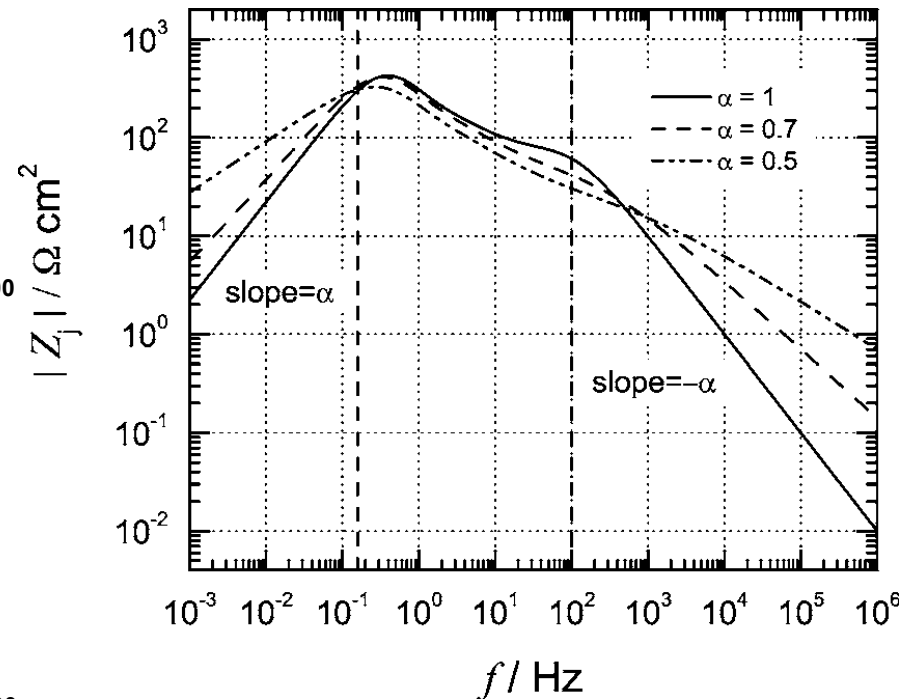
Graphical representations of EIS spectra

- Different, complementary information can be obtained by plotting the data in different forms, for example:

Bode plots of impedance:

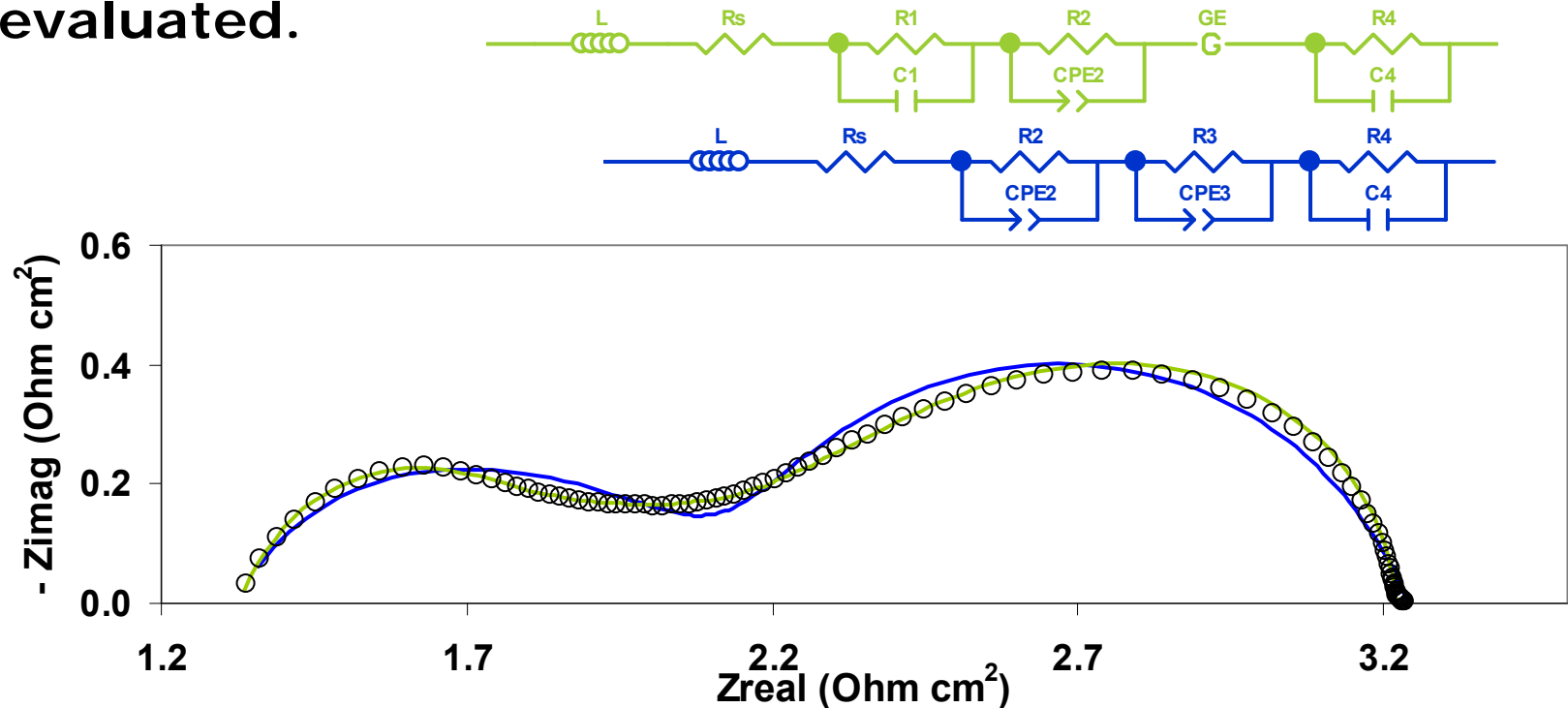


'logarithmic' Bode Plot

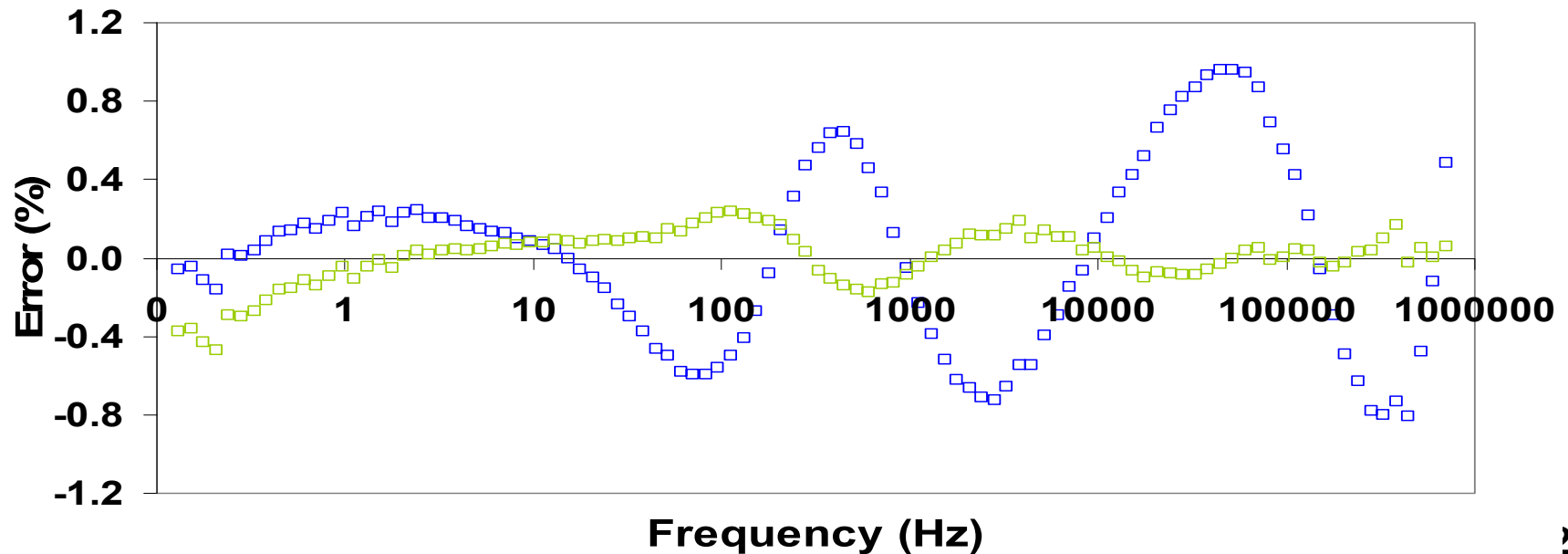
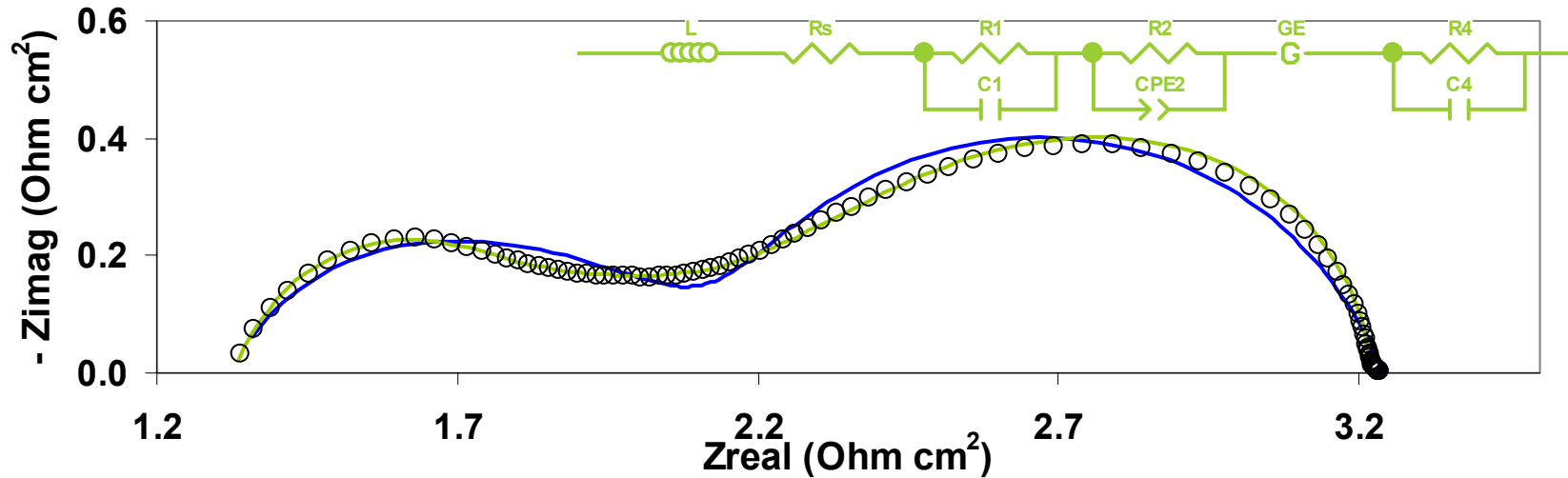
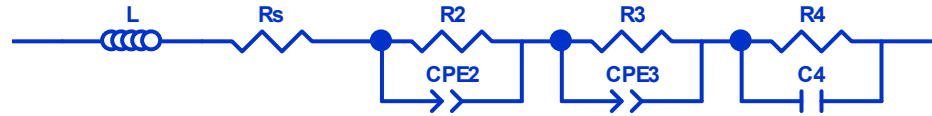


CNLS fitting

- When an equivalent circuit has been developed, the magnitudes of each of the elements can be calculated by CNLS fitting.
- By plotting the calculated values from the CNLS fitting, the 'goodness' of the equivalent circuit can be evaluated.



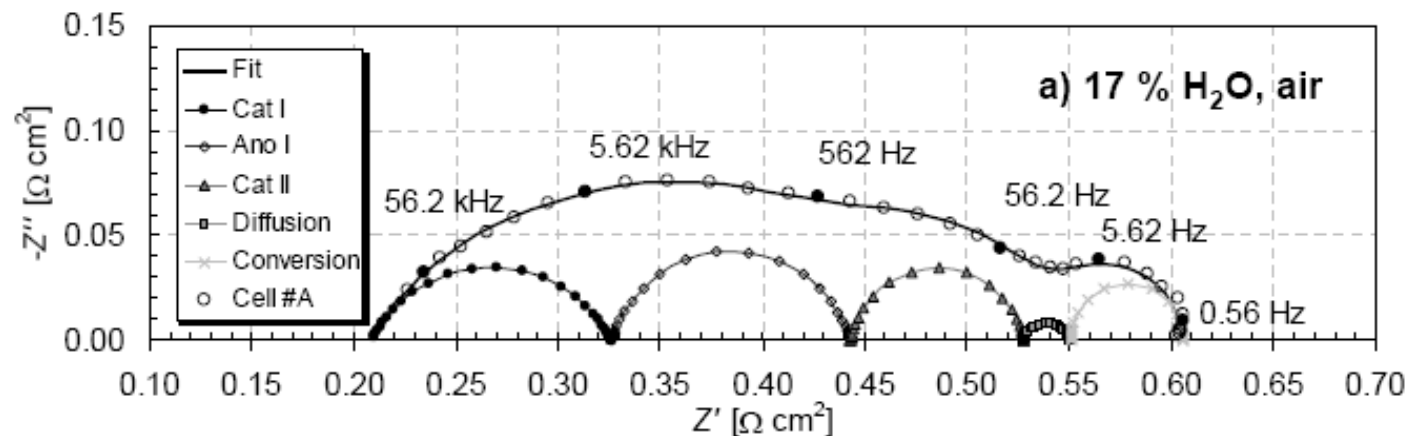
CNLS fitting



Break down of the cell impedance by fitting to equivalent circuits

A series resistance + 4(RQ) in series + (RC) in series!

As this can fit every elephant and octopus we must get a lot of pre-knowledge in order to do this in a credible manner



Ramos et al. 2008, ECS Transactions 13 235

Questions here?

My question to you: Any proposal about what to do in order to get this pre-knowledge?

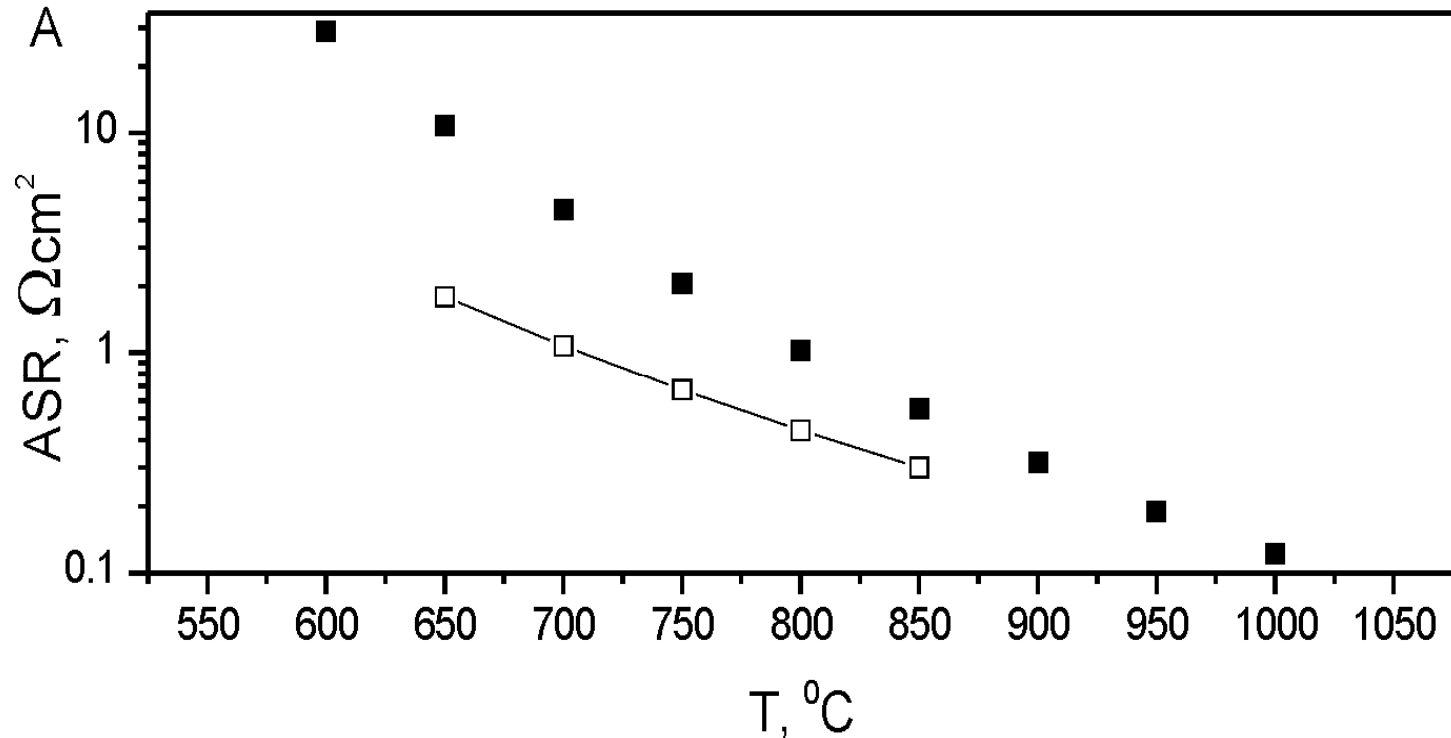
Electrode test strategies

- Naturally, we would like to measure all relevant properties of an electrode, e.g. electronic conductivity, ionic conductivity, electrocatalytic activity and electrochemical performance of a porous or even of a composite electrodes
- This cannot be done by testing of full cells. A rather tedious strategy is necessary

Specific SOC test problems

- The detailed structure of the solid oxide electrode is extremely important for the polarization resistance - this makes it difficult to assess the electro-catalytic effect of a potential electrode material using the technological type of composite electrodes
- Polarization resistance = overvoltage/current density ($\text{Ohm} \times \text{cm}^2$) is usually used instead of “overvoltage at a given cd” as SOC gives fairly linear responses
- For a given electrode - made as reproducible as possible - the polarization resistance may be very dependent on the thickness of the electrolyte and on the method of electrolyte fabrication

Specific SOC test problems



ASR measured on anode supported Ni/YSZ/LSM cells (open symbols, line) compared to ASR calculated from electrode and electrolyte data (closed symbols)

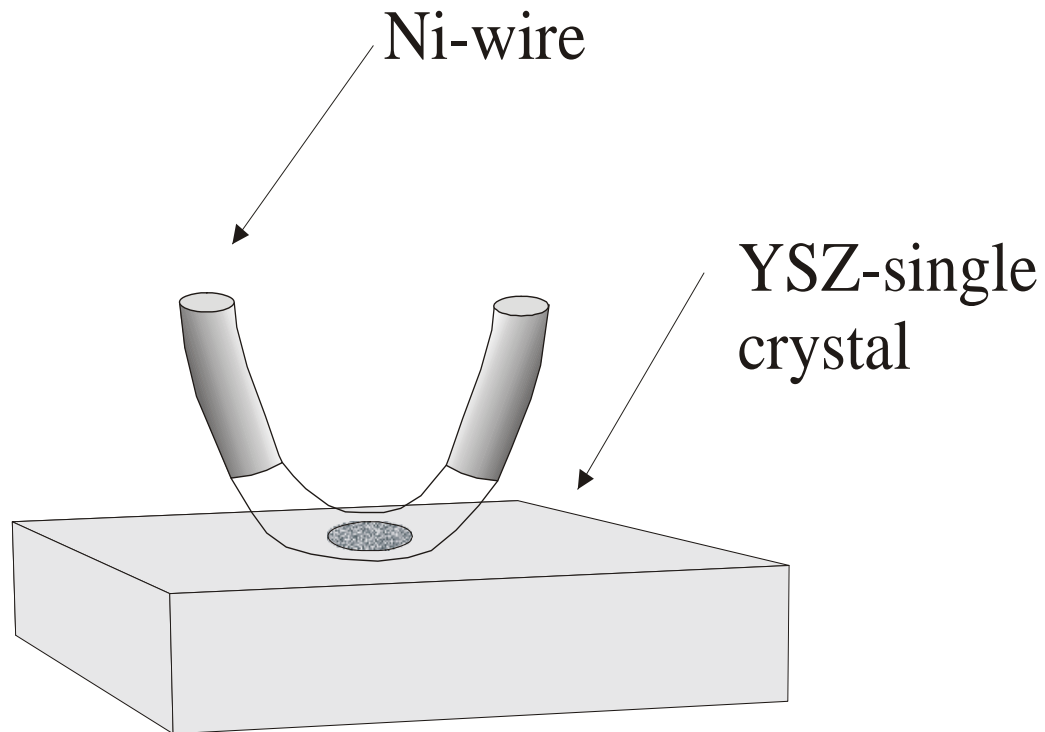
Test strategies

- It is necessary to use a number of set-ups - more or less a special set-up is required for each kind of property to be investigated
- Conductivity of materials may be measured in a classical 4-point set-up
- Electro-catalytic activity is tested using model electrodes
- Effect of structure may be tested in symmetrical 2-electrode cells
- Effect of overvoltage can only be studied accurately in a three-electrode set-up
- Measure EIS at many systematically varied conditions

Model electrodes

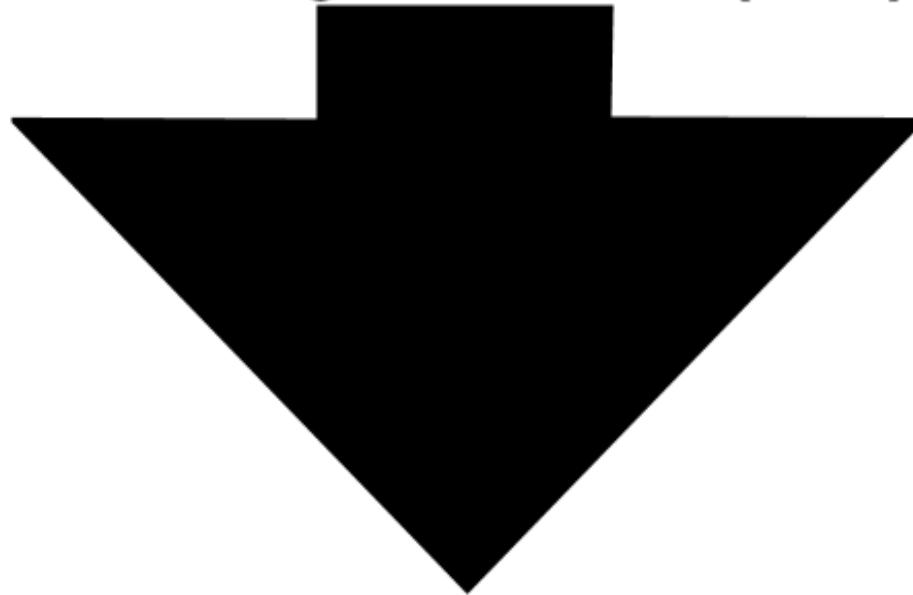
- Two main types
 - Pointed electrodes
 - Pattern electrodes
- The border line between them is not very sharp
- A “point electrode” may be defined as a circular (or elliptical) shaped contact, the radius of which is less than 0.1 times the thickness of the electrolyte
- The purpose of model electrodes is to know the exact contact area and three phase boundary length

"Point" electrodes of metal



Cone shaped "point" electrode of ceramics

Working electrode (WE)



YSZ

Counter electrode (CE)

Point electrode

The area can be determined/estimated by

$$r = \frac{1}{4 \cdot \sigma \cdot R_s}$$

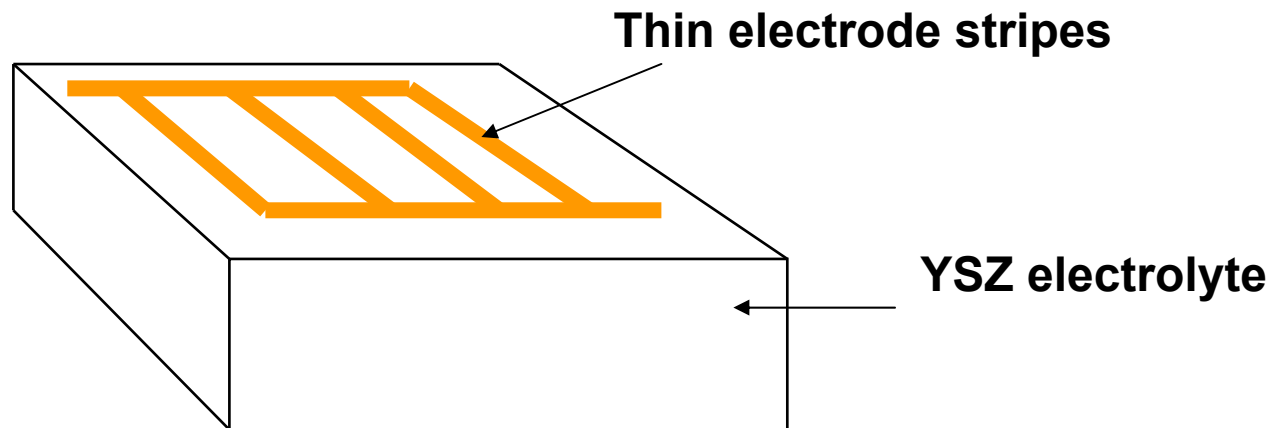
r is the radius, σ is the specific conductivity of the electrolyte material and R_s is the series resistance

Thickness, t , of electrolyte: $t > 10r$

Model electrode

- Determination of the electro-catalytic activity (for given geometry and conditions) is possible in principle
- $1/R_p$, where R_p is the polarization resistance, is a measure of the specific electro-catalytic activity for the electrode material in case of a well-defined electrode geometry
- The surface topography (and other surface properties) of both electrolyte and the electrode must be carefully controlled
- This means that it may be only possible in practice for a series of ceramic materials if the preparation of the cone electrodes is done by the very same person
- Dots made by e.g. pulsed laser deposition may be more reproducible (and have other problems)

Pattern electrodes



Also a counter and a reference electrode must be applied (not shown)!

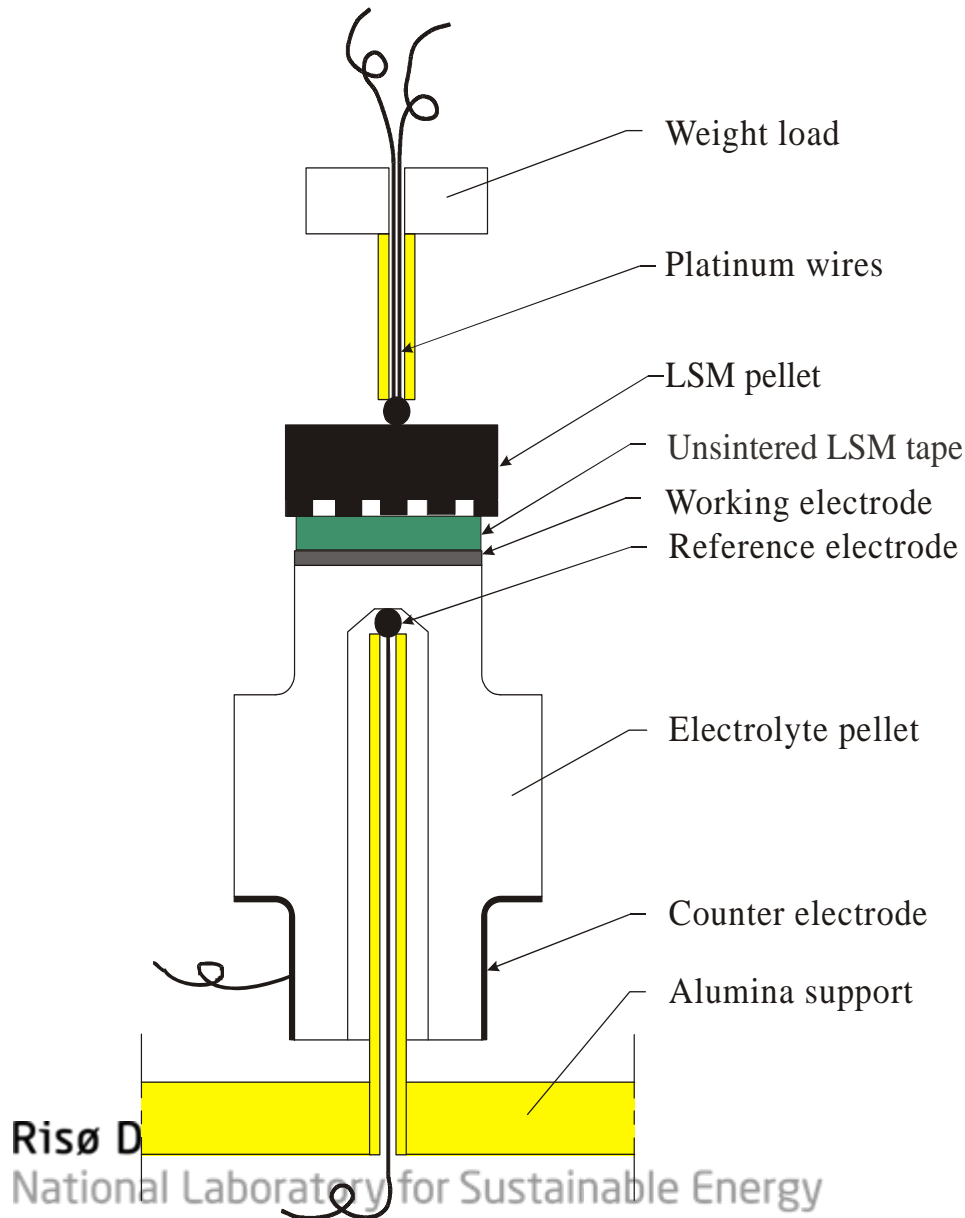
Tests of technological electrodes

Technologically relevant electrodes are usually composites e.g. Ni-YSZ and LSM-YSZ

- 3-electrode cells
- symmetric cells
- full cells

All have their advantages and disadvantages

Three-electrode-set-up

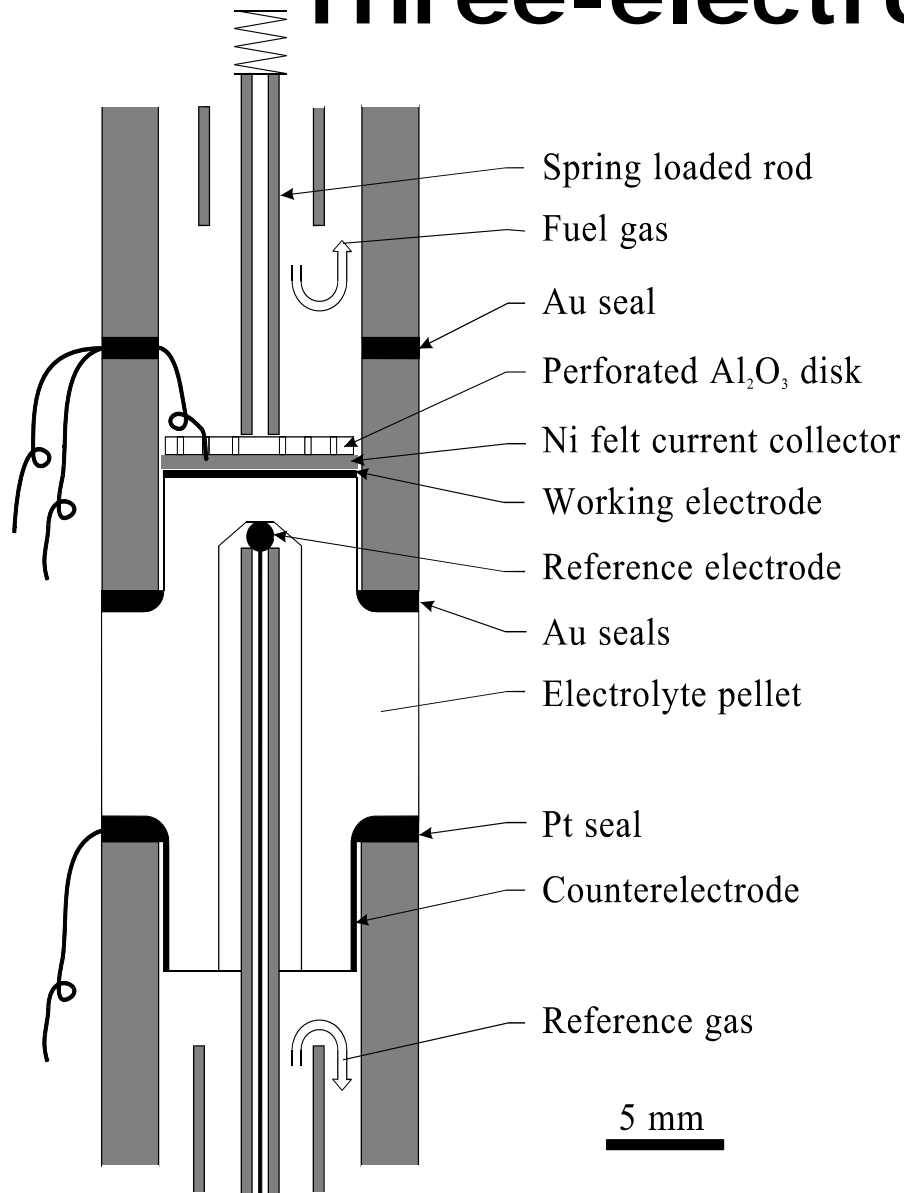


The Risø 3E-pellet is a proper 3E-set-up, but there are other possibilities

It must be a thick electrolyte, a pellet like thing in case of good electrodes

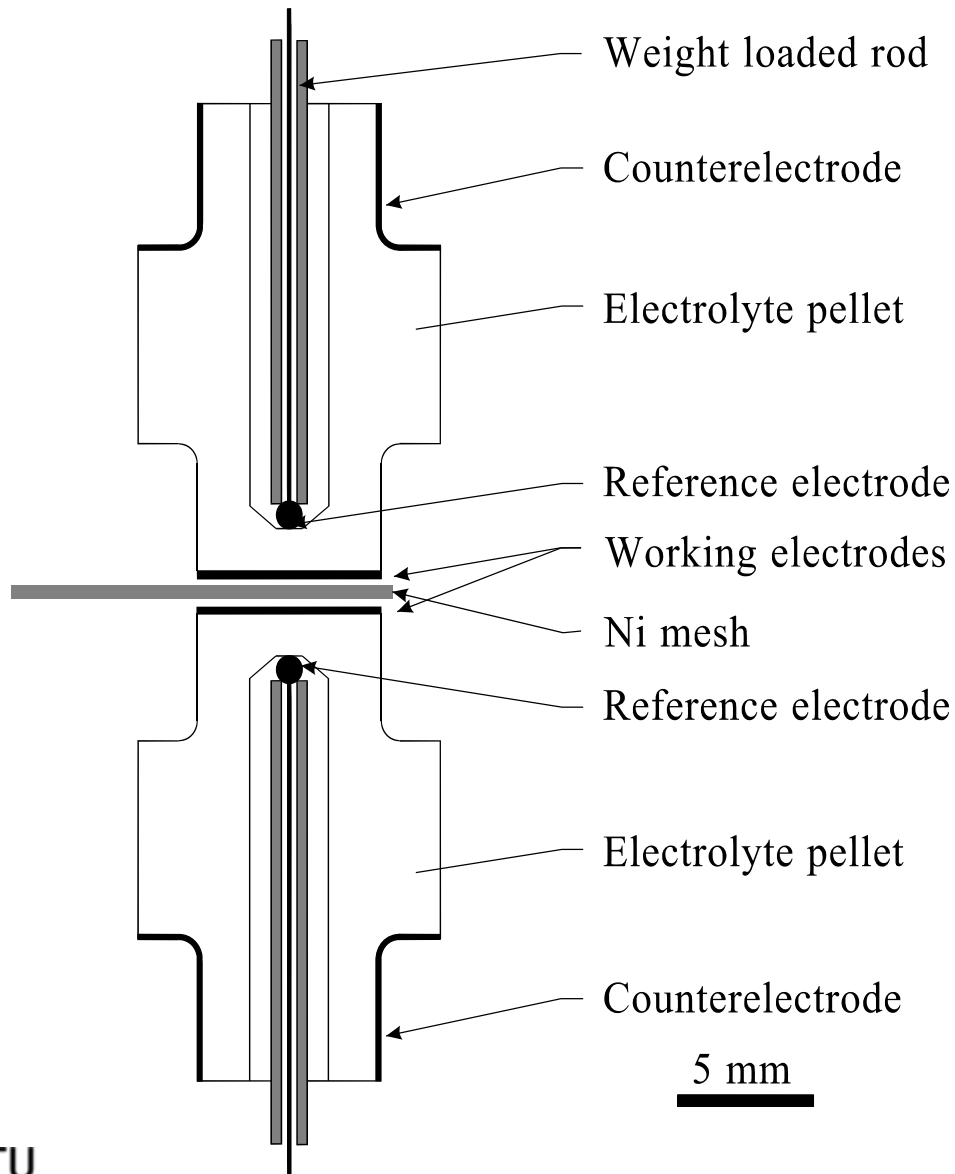
Ref.: Winkler, Hendriksen, Bonanos, Mogensen, *Geometric requirements of solid electrolyte cells with a reference electrode*, J. Electrochem. Soc. **145** (1998) 1184-1192

Three-electrode-set-up



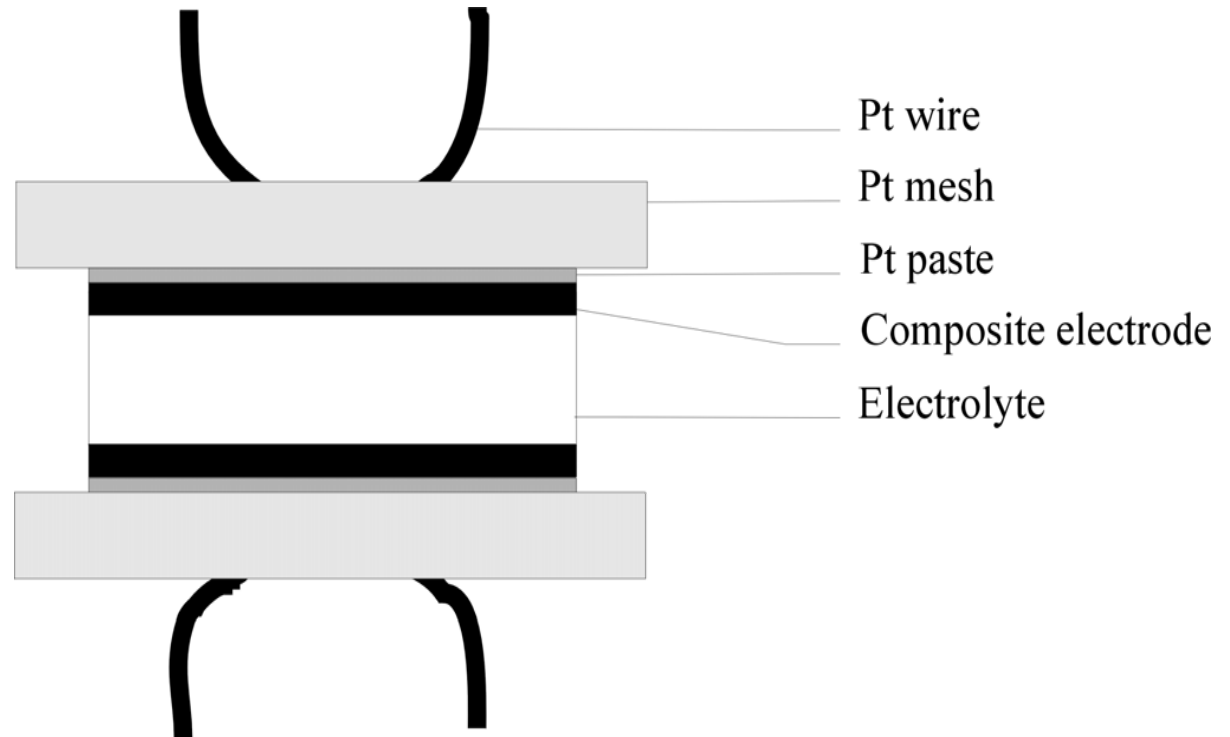
Real reference electrode – If e.g. pure oxygen is reference gas, the reference electrode potential is constant

Three-electrode-set-up



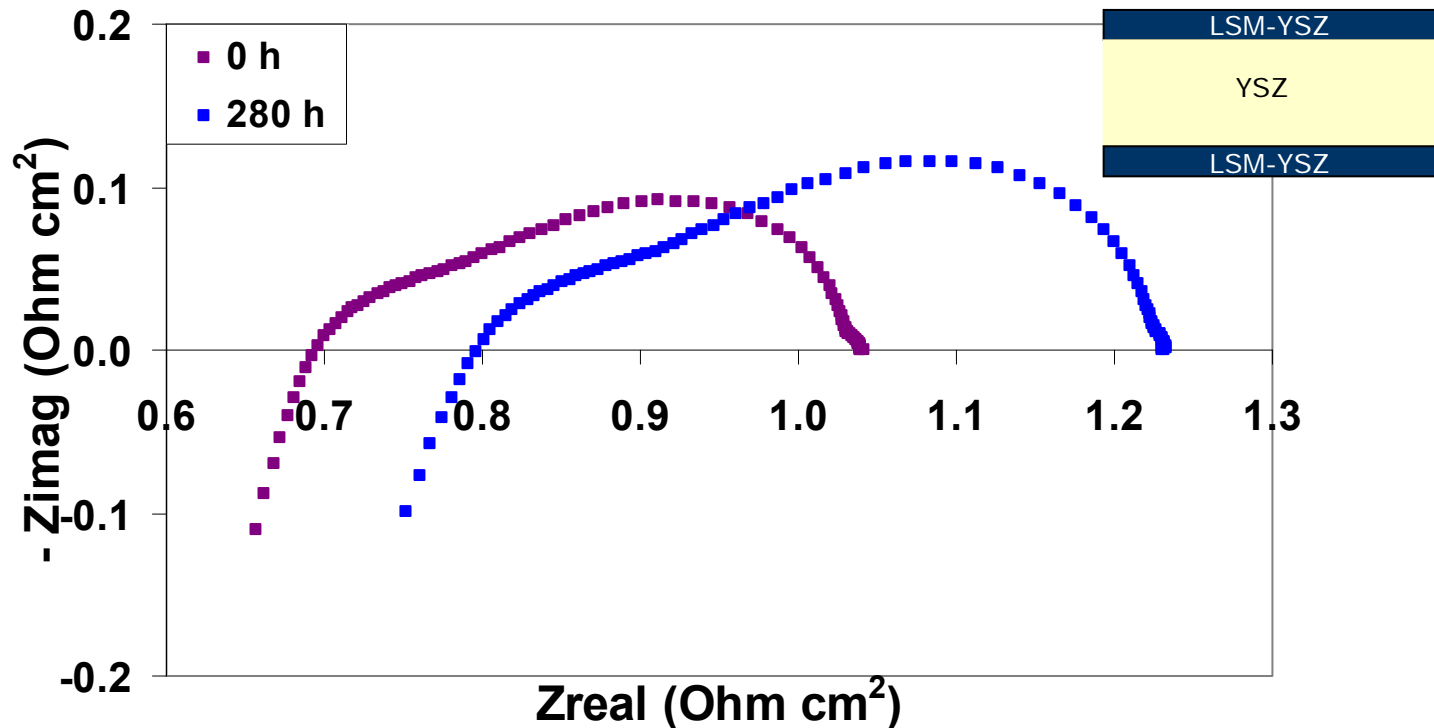
One of them to be used as an auxiliary electrode

Symmetrical cell

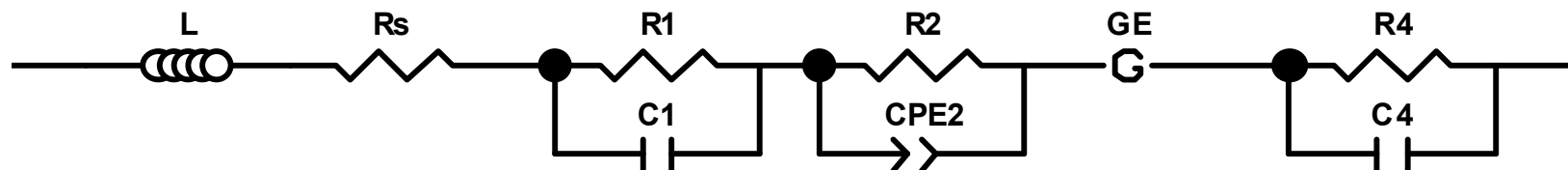


A symmetrical two-electrode cell arrangement for measurements at OCV

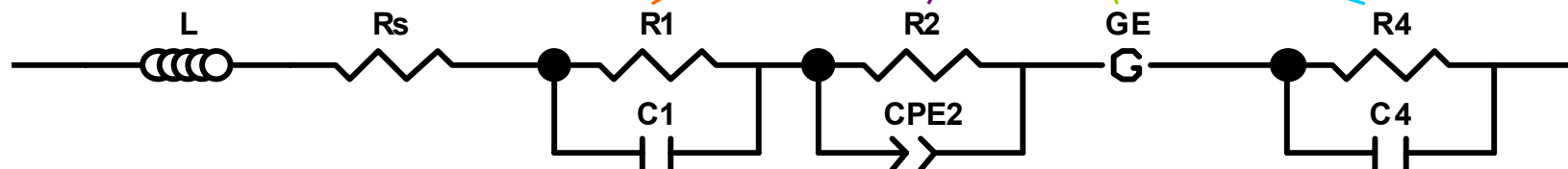
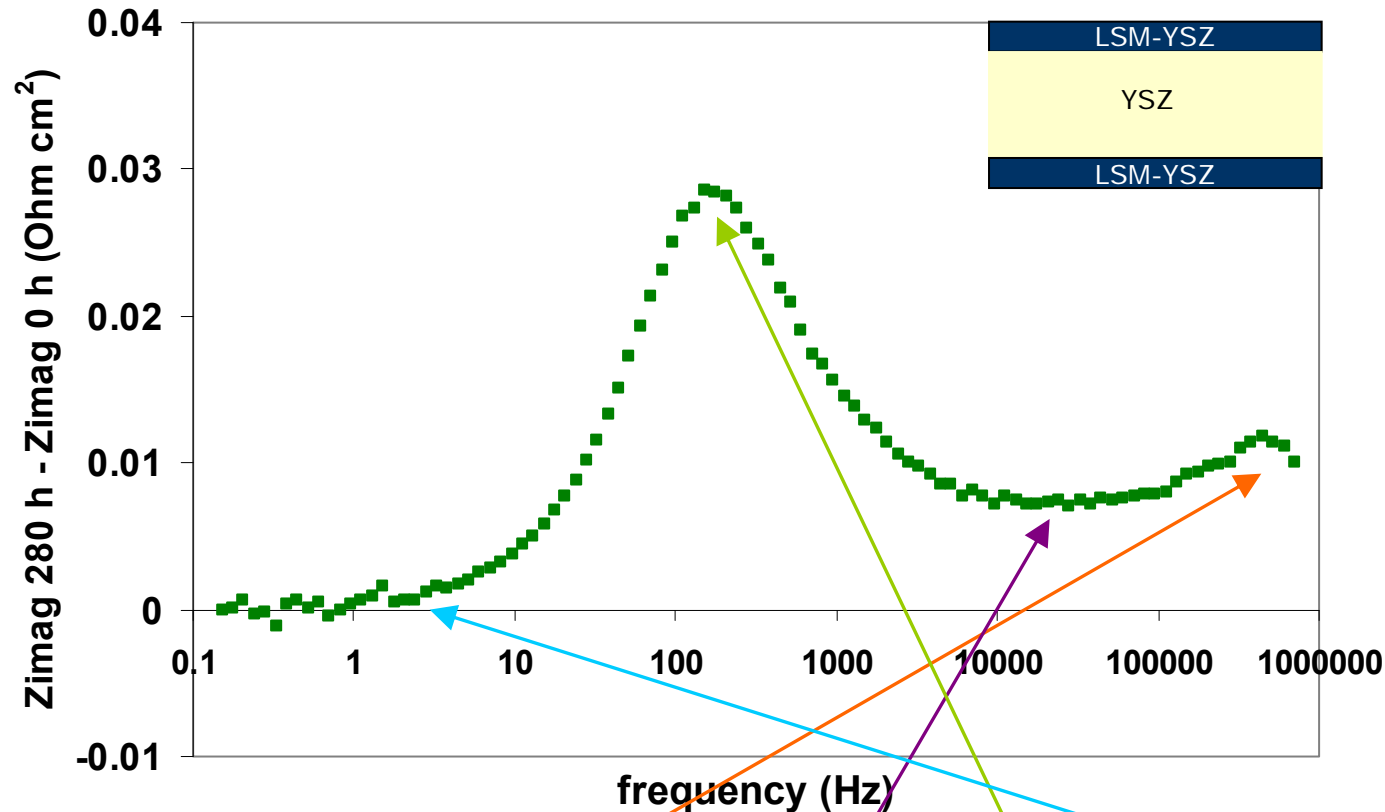
Degradation/deactivation of symmetrical solid oxide cells



Equivalent circuit:



Degradation/deactivation of symmetrical solid oxide cells



Symmetric cell data

For both symmetric cell with SOFC anodes and cathodes two ion transfer related arcs have been observed in the EIS. An example of data seen below.

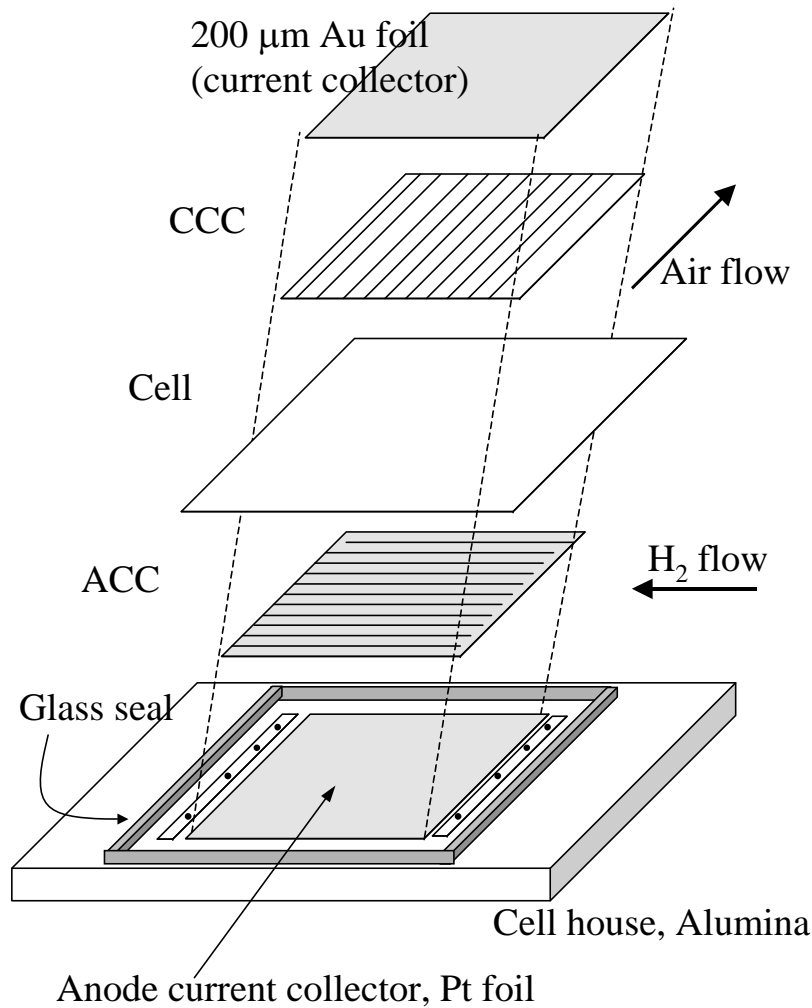
f_{summit} [Hz]	850°C	750°C	650°C
Anode 1 (?)	34,500	22,700	7,360
Cathode 1	26,100	26,100	8,254
Anode 2	4,390	1,510	337
Cathode 2	2,610	825	26

Full cell vs. symmetric cells

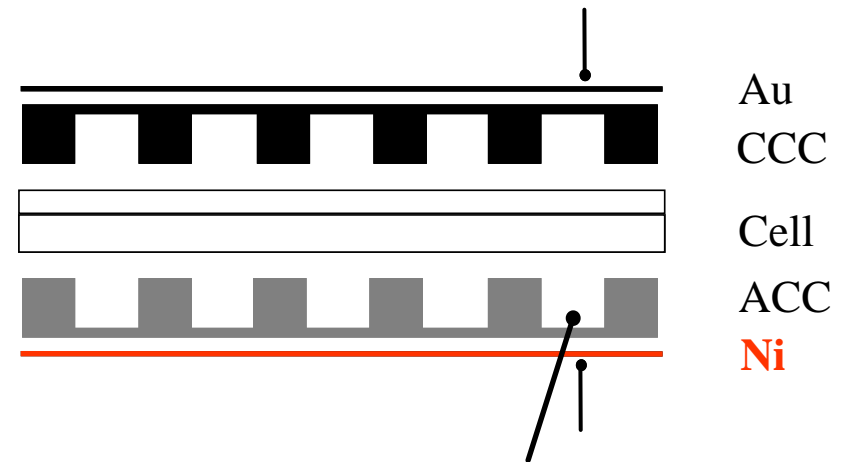
Temperature °C	Conditions Air &	Full cell B Anode [$\Omega \text{ cm}^2$]	Sym. cell Anode [$\Omega \text{ cm}^2$]	Full cell B Cathode [$\Omega \text{ cm}^2$]	Sym. cell Cathode [$\Omega \text{ cm}^2$]
750	20% H ₂ O	0.09	0.23	0.24	0.30
	3% H ₂ O	0.16		0.26	
650	20% H ₂ O	0.46	1.05	0.87	1.32
	3% H ₂ O	0.60		0.90	

- Symmetric cells exhibit consistently higher resistances
- The summit frequencies are generally higher in full cells
- The differences are more marked for the anode
- What justifies these differences? Production? Different amounts of impurities? Overall different microstructure? Intrinsically different test setup? Combination of previous?

Full cell test

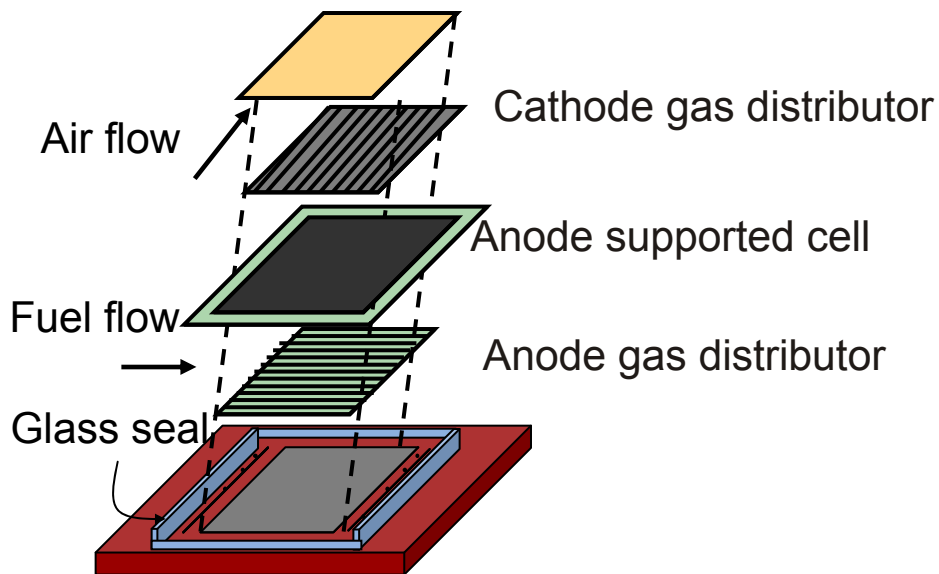


5x5 cm foot print
4x4 cm active area



A cell test strategy

1. Full cell test



Old Risø set-up: Active cell area: 16 cm².

Many other set-ups are possible

2. Fingerprinting with gas (anode and cathode) and current variations

- EIS (e.g. OCV, 0.25 & 0.5 Acm⁻²)
- i-V curves
- Fuel gas: p_{H₂O}/p_{H₂} from 0.04 to 1.00 at constant total flow
- Cathode gas: dilution series (pO₂ from 0.02 to 1.00) at constant total flow

3. Symmetric cell testing

To get the single electrode EIS response

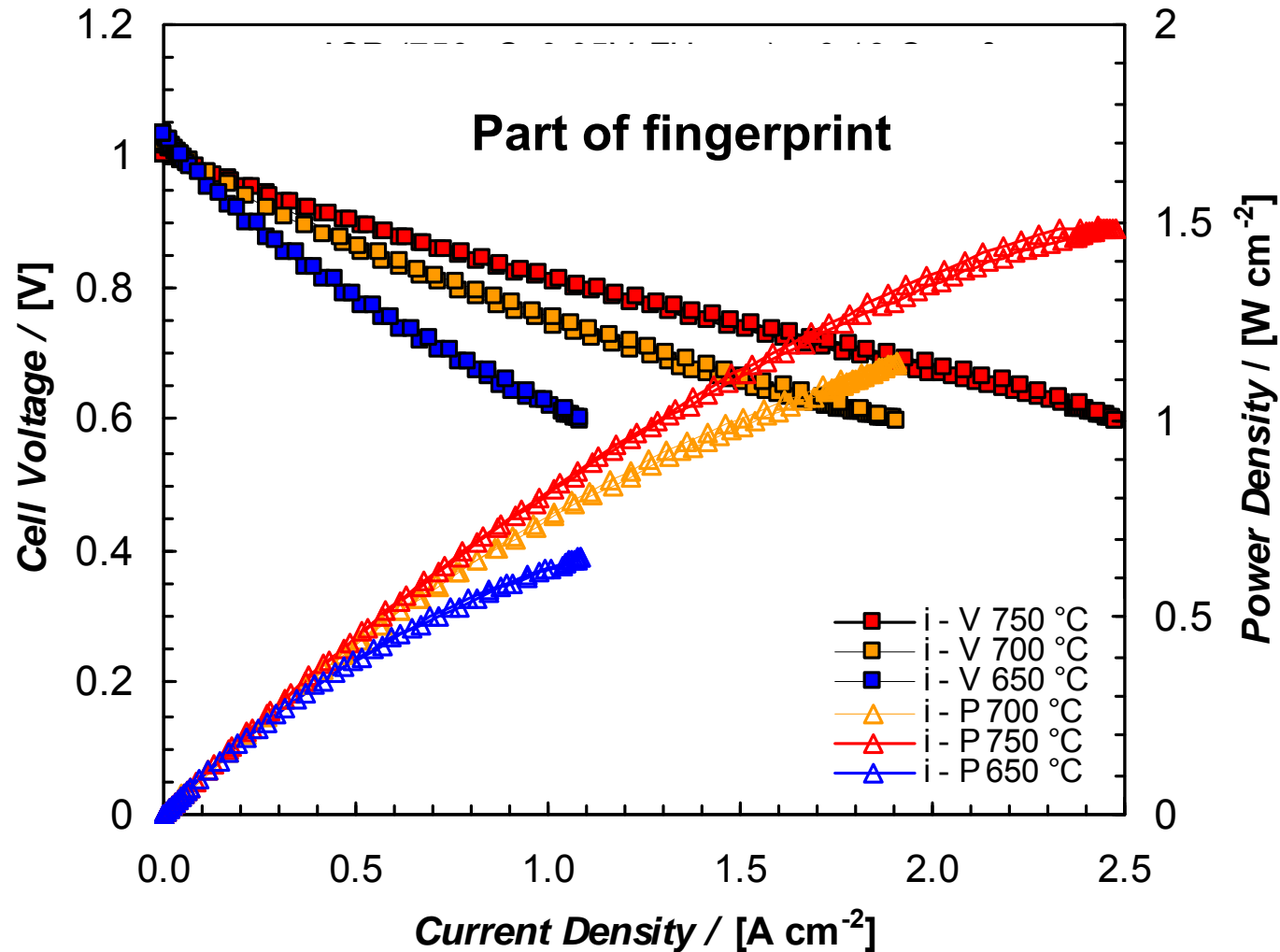
4. Data analysis

- ADIS
- DRT
- CNLS approximation to a model function (equivalent circuit)

Purpose of "fingerprint"

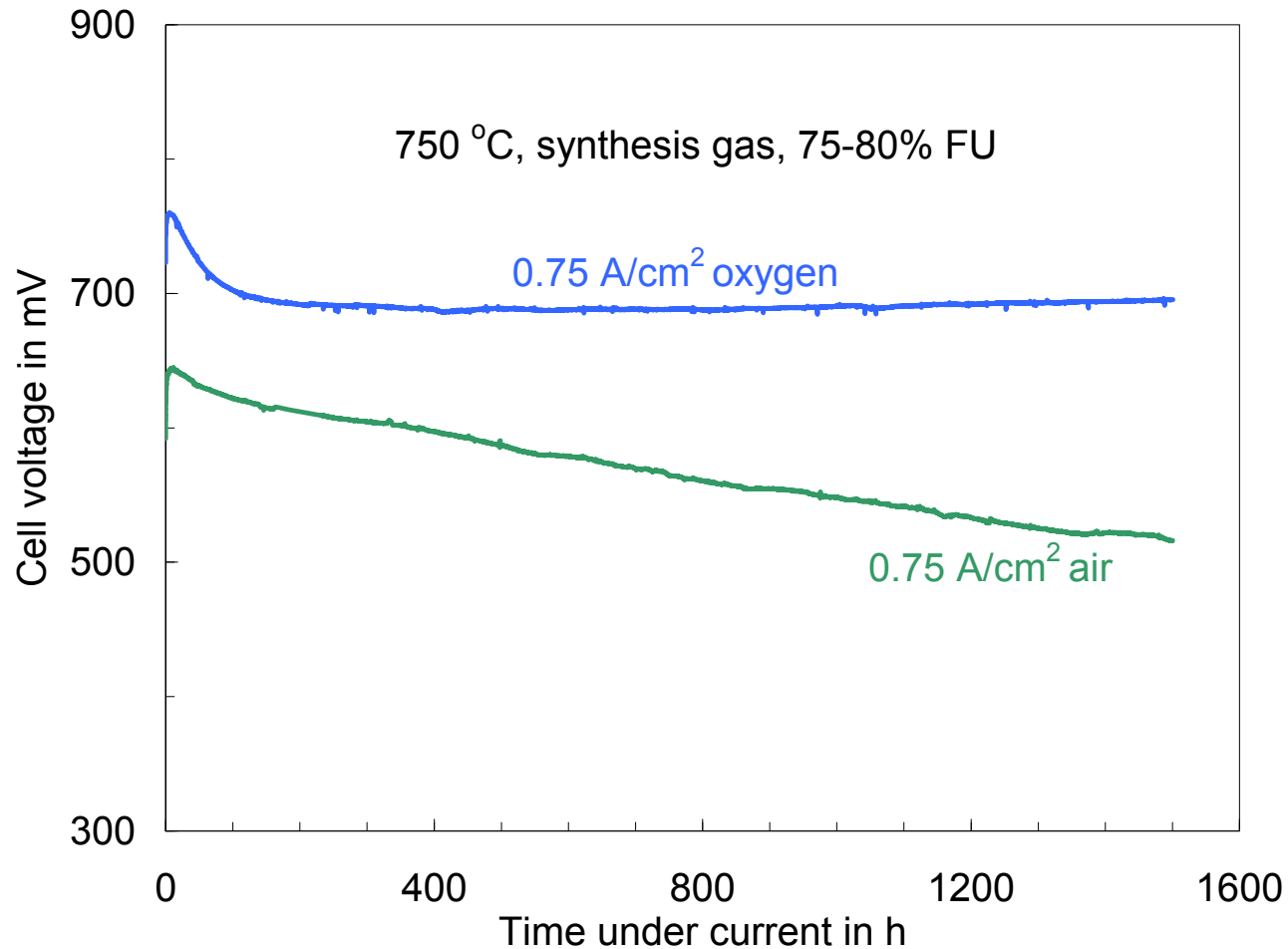
- If used on all cells then it is possible to compare the start performance of all cells
- If the fingerprint is used again at the end of say a durability testing then the changes can be described in much more detail than a change in potential at a given current density

Cell performance



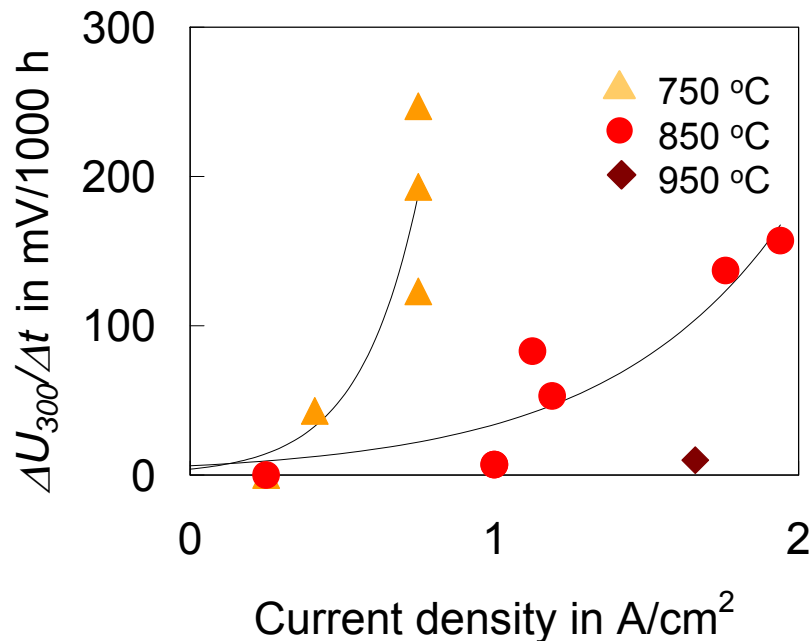
i - *V* and *i* - *P* curves for a Risø SOFC anode supported Ni-YSZ/YSZ/CGO/LSC-CGO cell

SOFC (Ni-YSZ-LSM) degradation

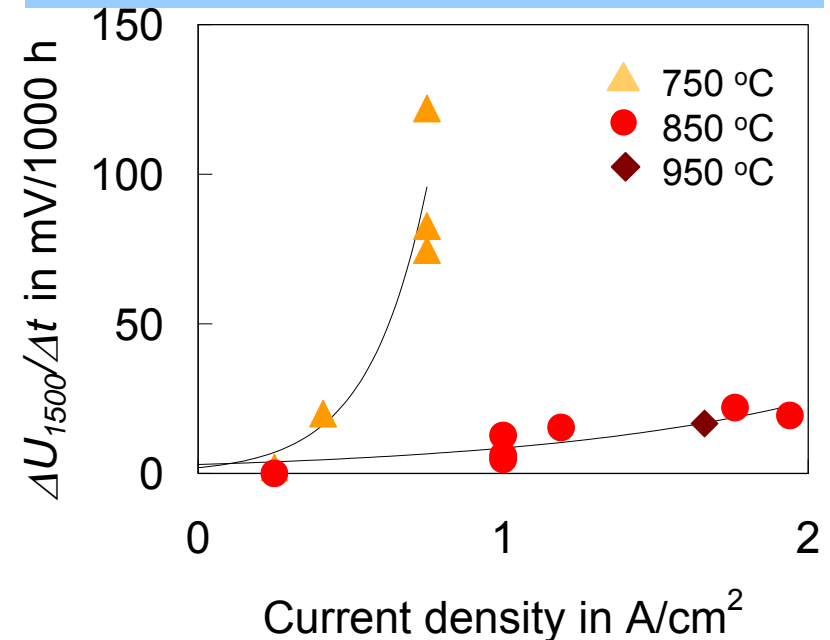


Ni-YSZ/YSZ/LSM-YSZ: Degradation rates vs. current density

After 300 h operating time - mainly reflecting anode degradation



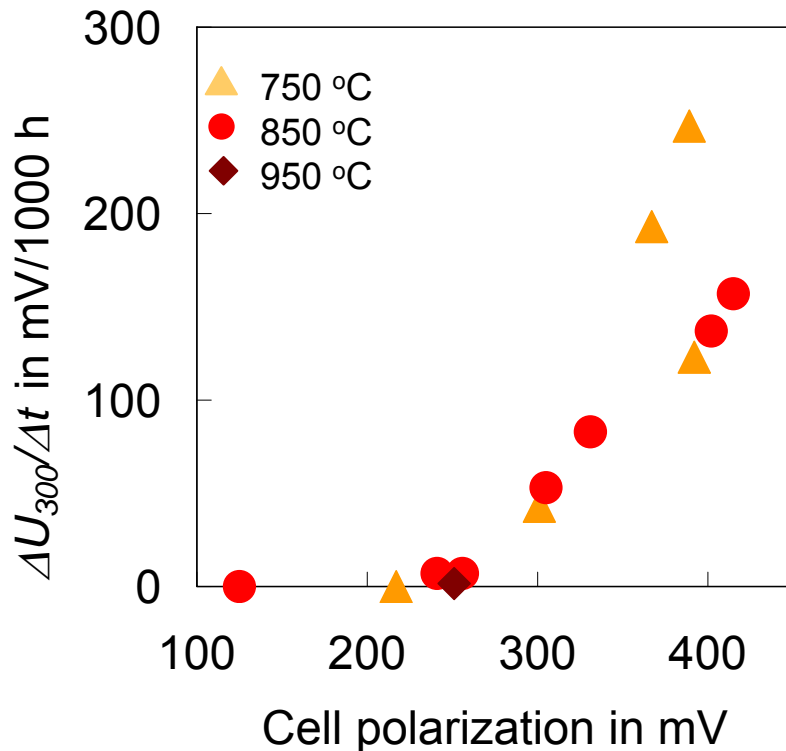
After 1500 h operating time - mainly reflecting cathode degradation



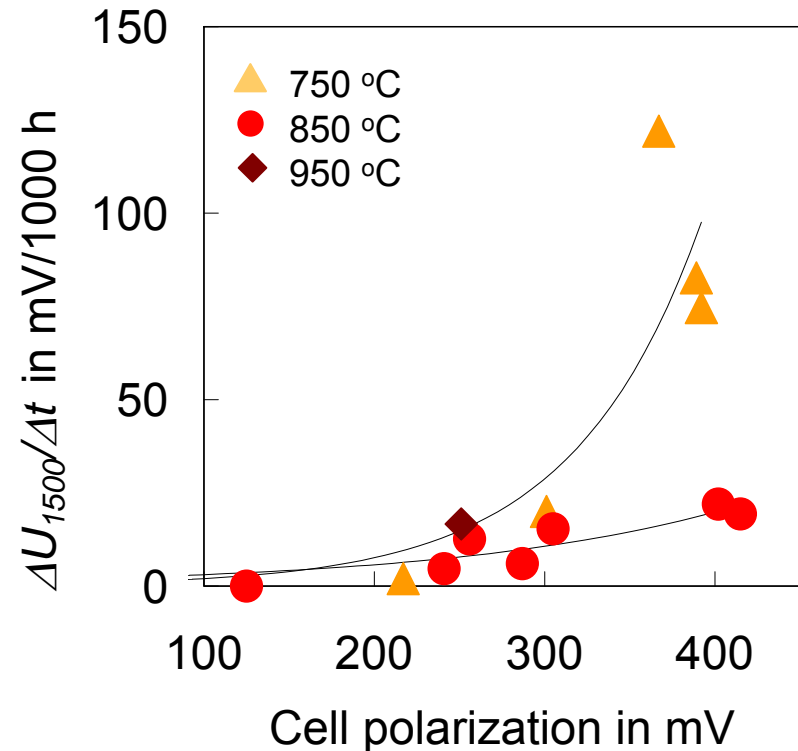
This and following are from A. Hagen et al., J. Electrochem. Soc., 156 (2006) A1165 – A1171, and SOFC-X, 2007, Nara, Japan

Degradation vs. cell polarization

After 300 h operating time - mainly reflecting anode degradation

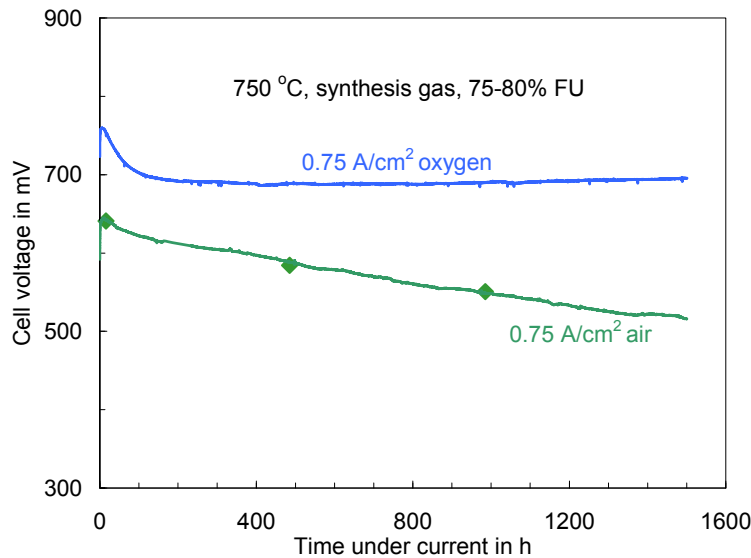


After 1500 h operating time - mainly reflecting cathode degradation



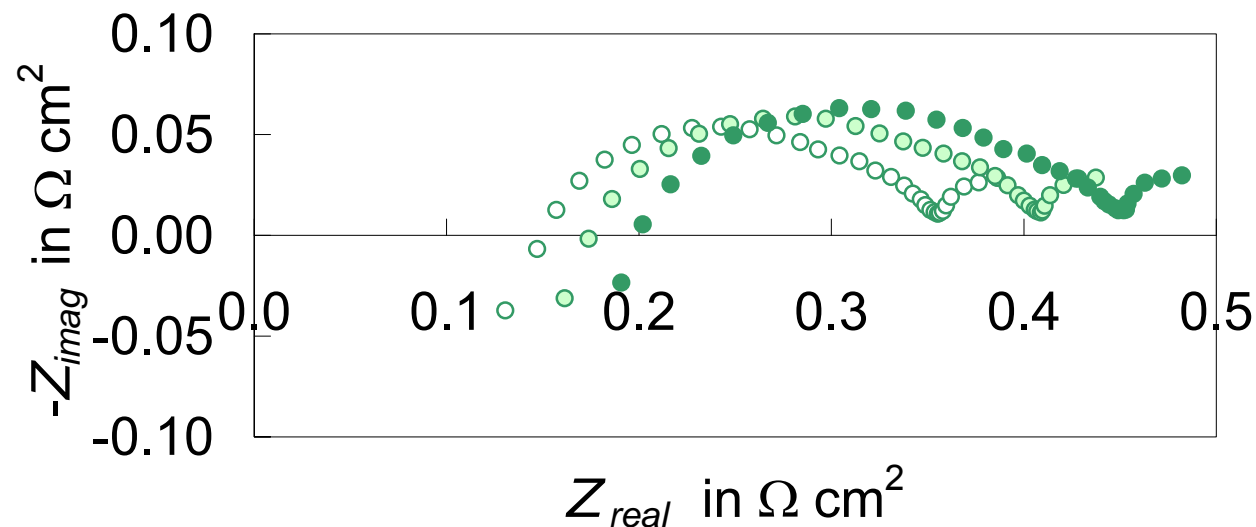
- Anode (300 h): Degradation rates nearly same at all temperatures (except at high polarization)
- Cathode (1500 h): Degradation rates at 750 °C much larger than at the higher temperatures

Impedance spectra under polarization: Test in air

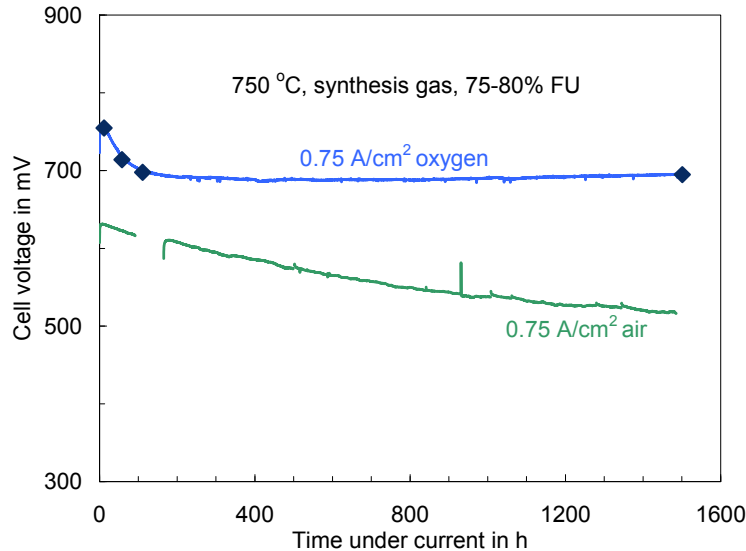


Air:

- Continuous increase of both, serial and even more polarization resistance over 1500 h

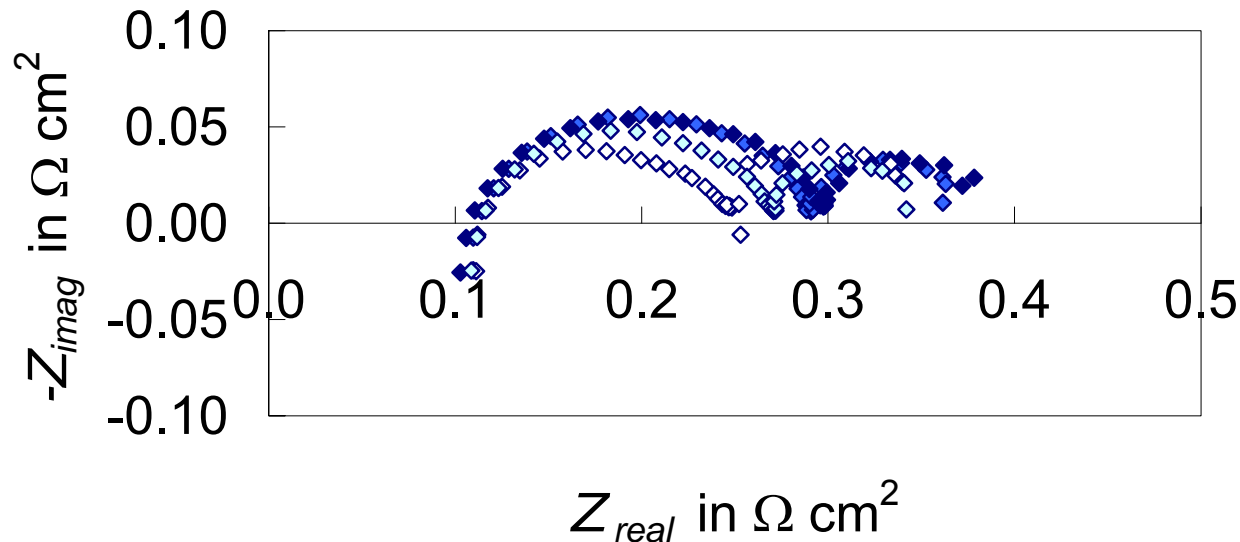


Impedance spectra under polarization: Test in oxygen



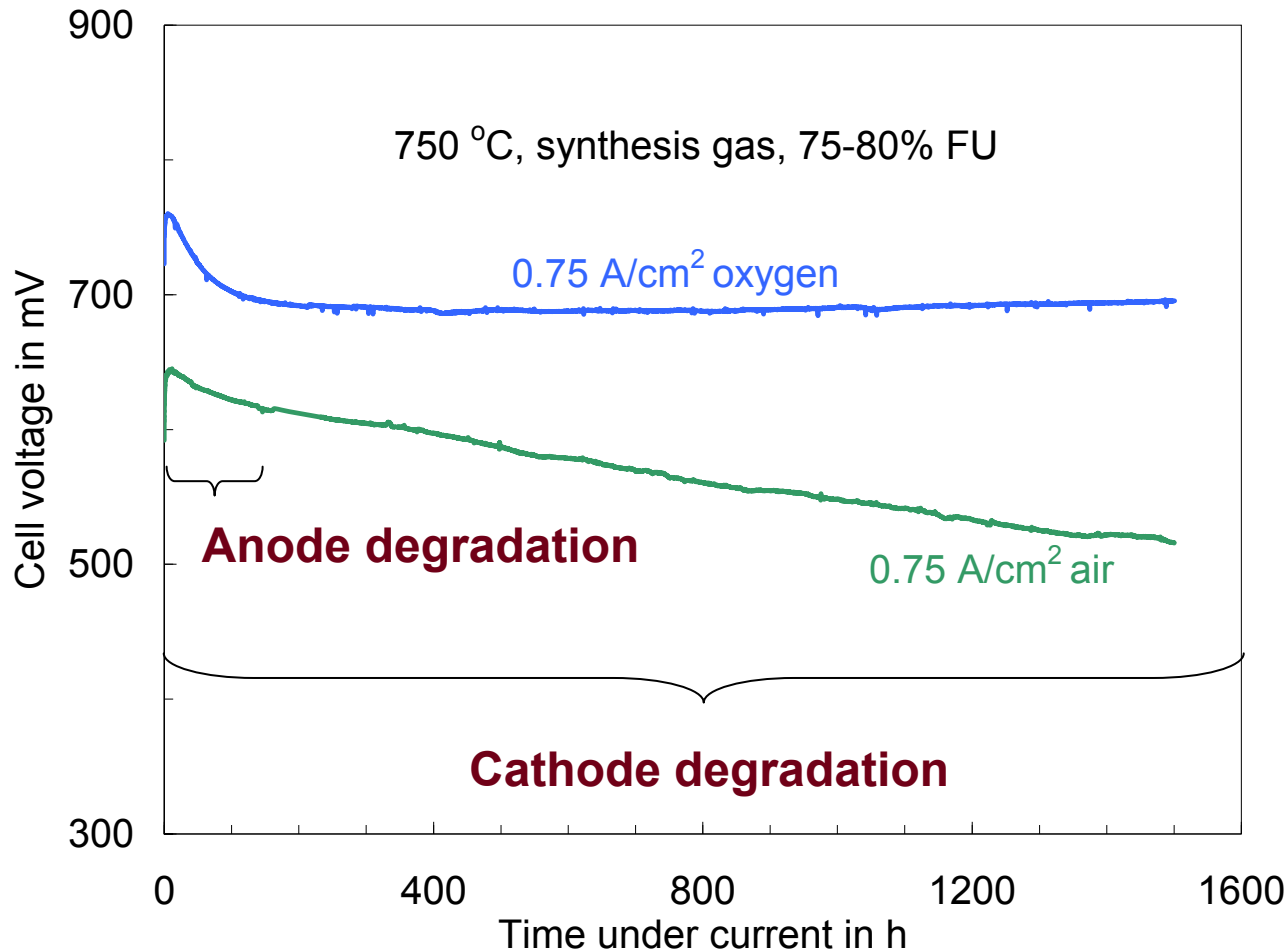
Oxygen:

- Almost constant serial resistance
- Increase of polarization resistance only within the first ~100 hours, afterwards no changes until 1500 h

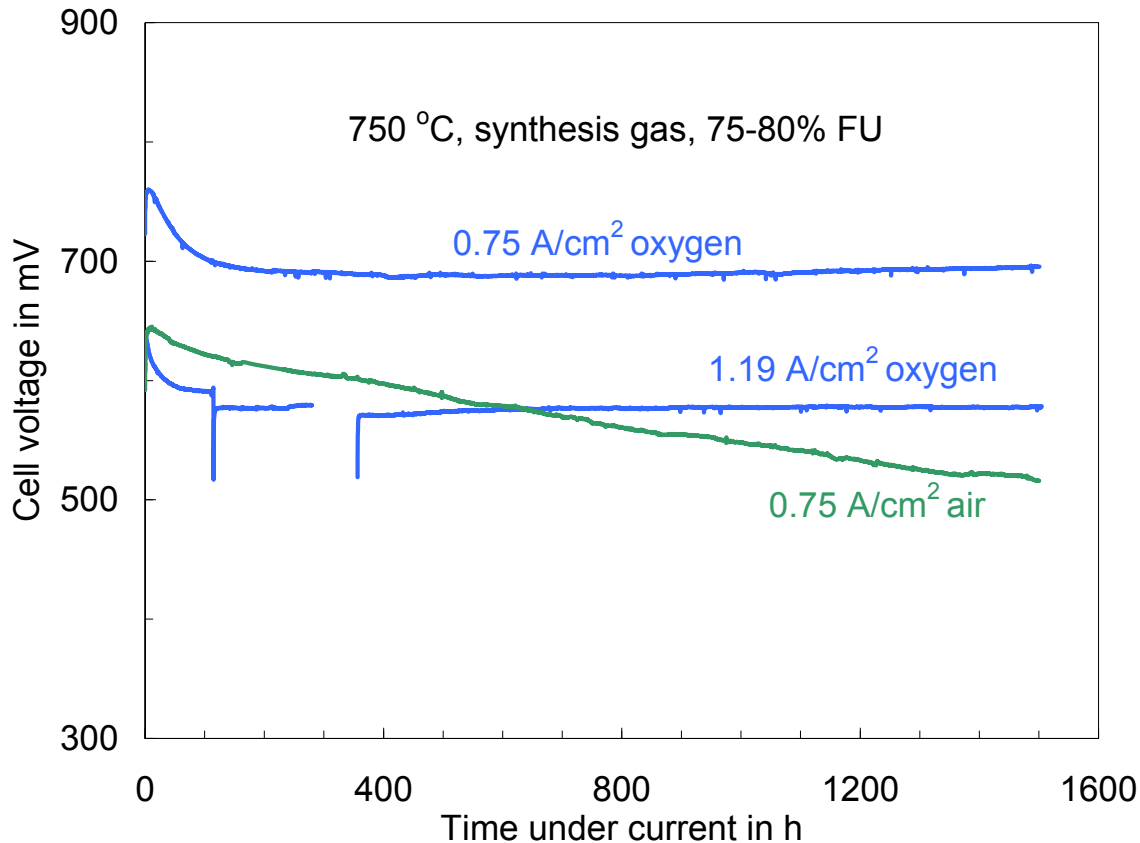


SOFC anode and cathode degradation

Impedance spectroscopy tells us which electrode that degraded how much after a given test time



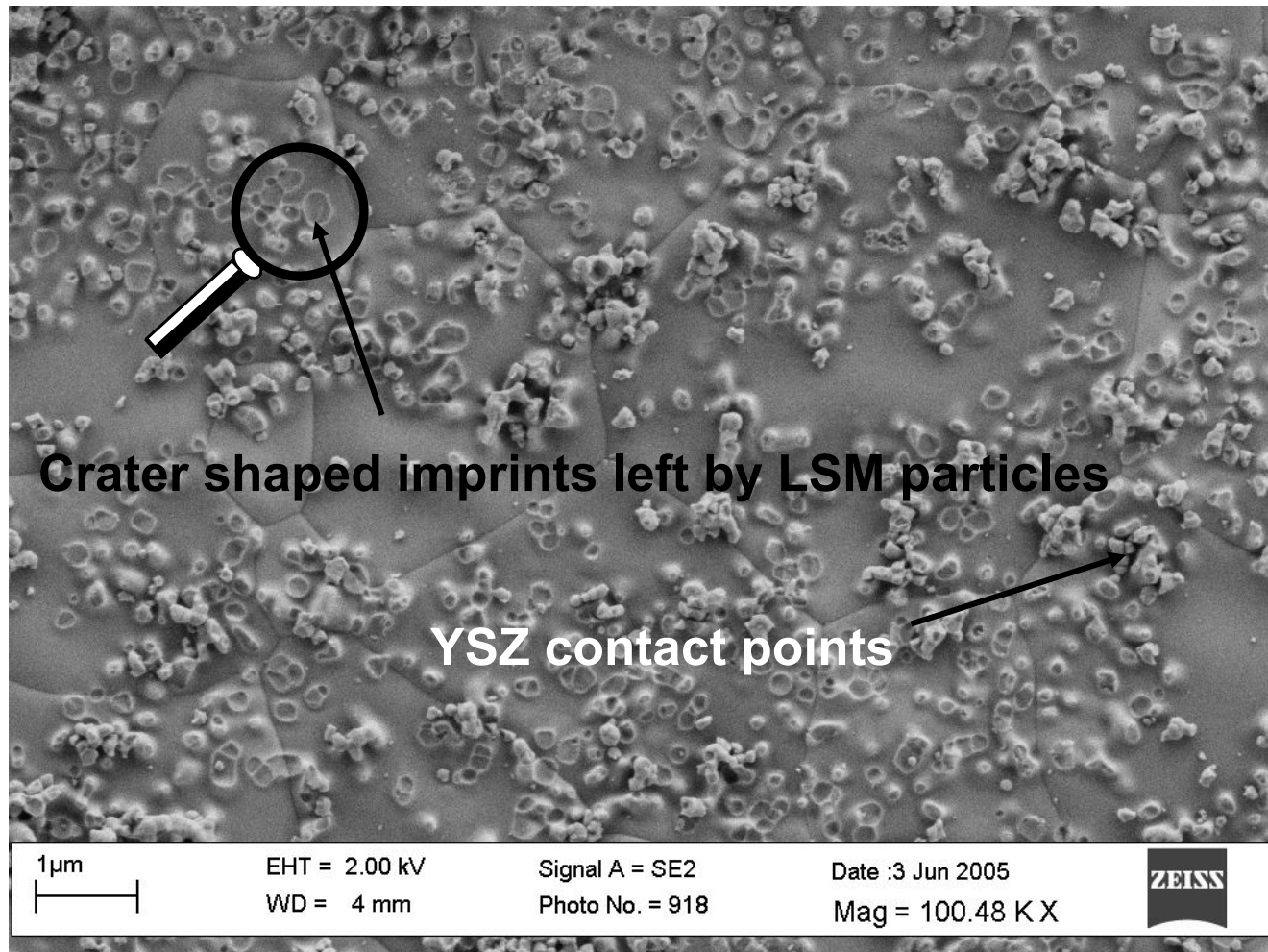
Degradation of cell voltage - effect of pO_2 and cell voltage



Apart from the fast initial degradation over first hundred hours (anode) no degradation until at least 1500 h is observed, i.e. no cathode degradation in pure oxygen, at these conditions

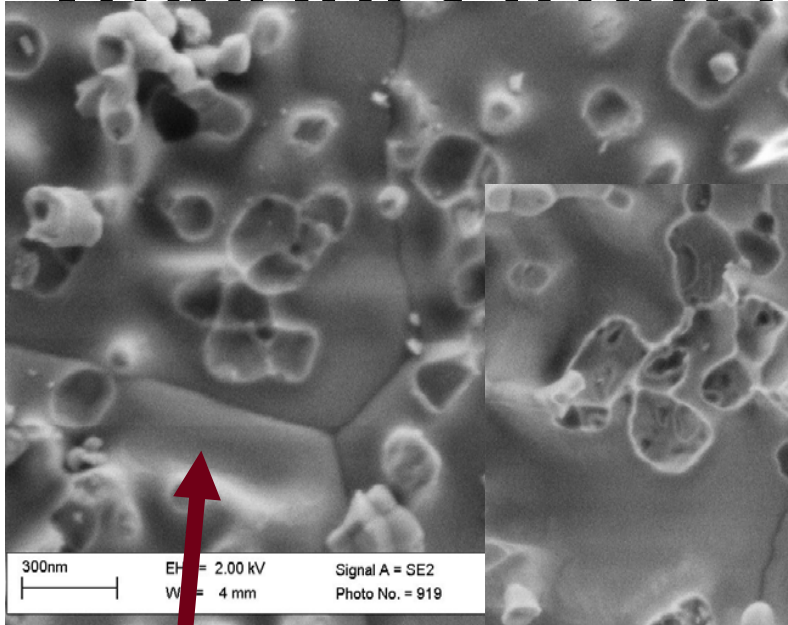
Post-test microscopy: Removal of cathode

View on electrolyte surface after etching cathode away

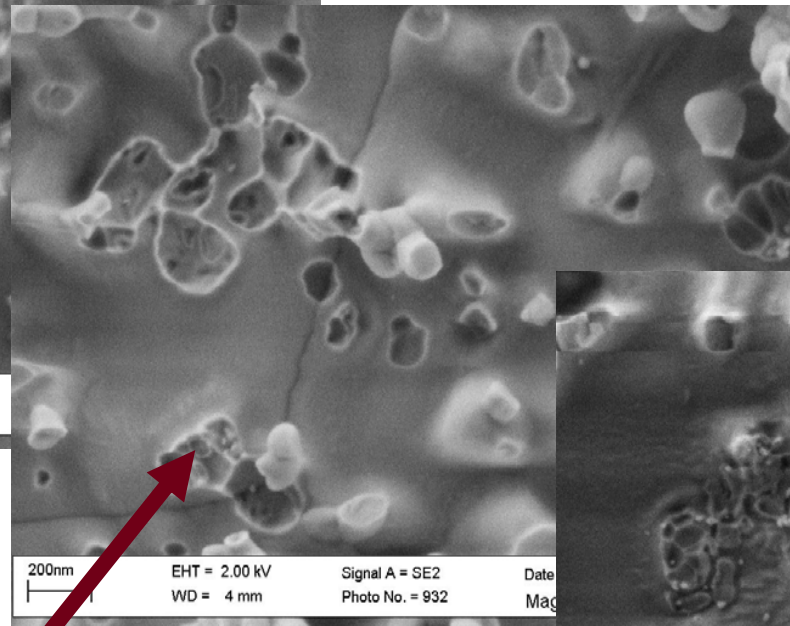


Post-test microscopy: Imprints from I.S.M on electrolyte

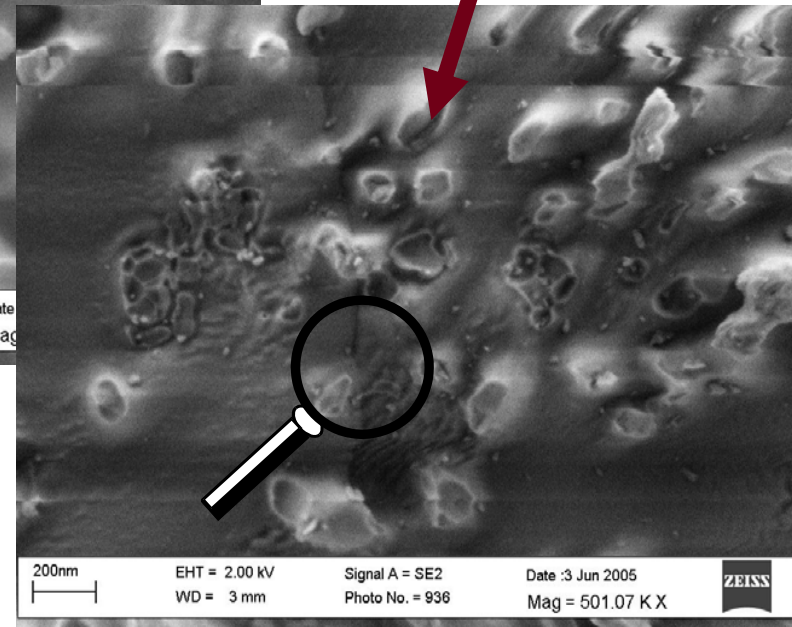
Small, blurred craters,
wrinkled surface after
test in air



Reference cell



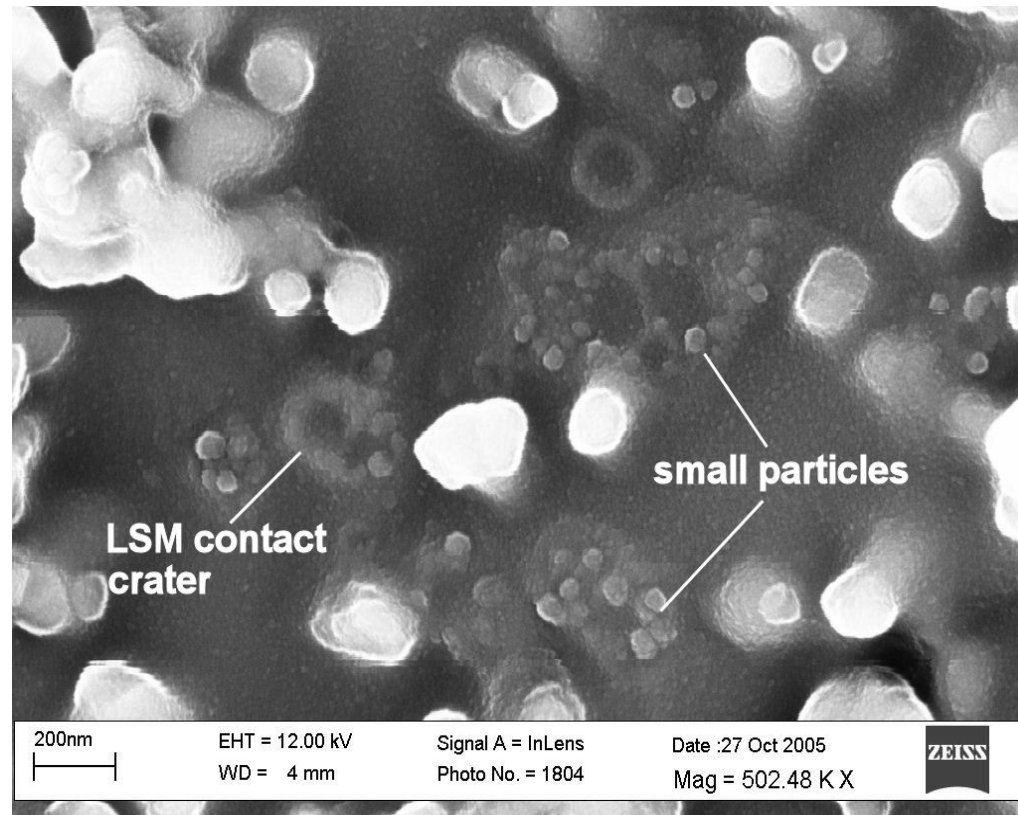
After test in oxygen



SOFC Summer School 2010
After test in air

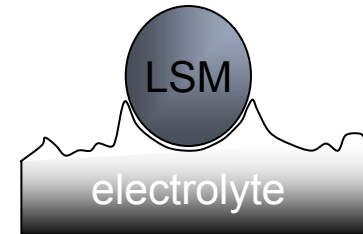
Sharp craters on reference
and after test in oxygen

Post-test microscopy: Cell tested in air

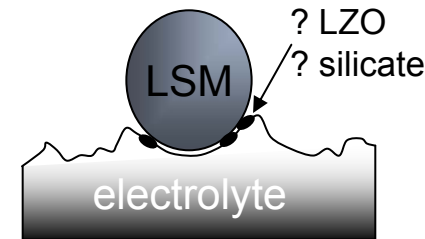


Degradation mechanism on the SOFC cathode at 750 °C

Reference cell



After test in air



Under reducing conditions at the LSM:

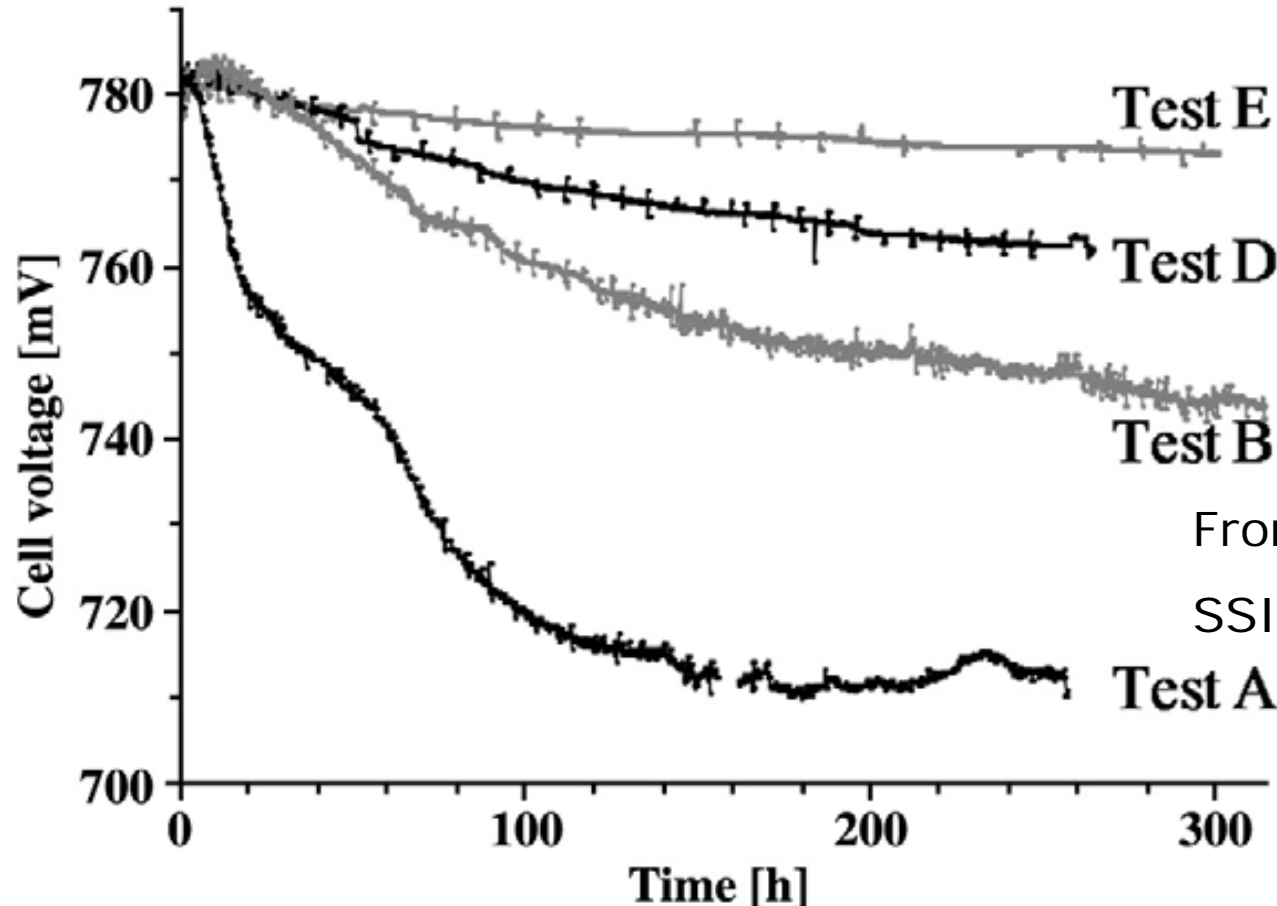
- **Redistribution of elements in LSM/electrolyte interface region under conditions of high cathode polarization and low oxygen activity**
- **Formation of nano-sized particles of isolating foreign phases (LZO, silicates?)**
- **Weakening of contact between LSM and electrolyte**

This is in good accordance with M. Chen et. al., O 268

Effects of impurities on the TPB

- Many impurities (incl. H_2O) may degrade the electrode performance, e.g.
- H_2O in case of some LSM type of cathodes
- CrO_3 vapour and other Cr (VI) containing vapours
- High pH_2O in the Ni-YSZ anode
- Sulphur containing electrodes
- + + +

Durability as f(test details)

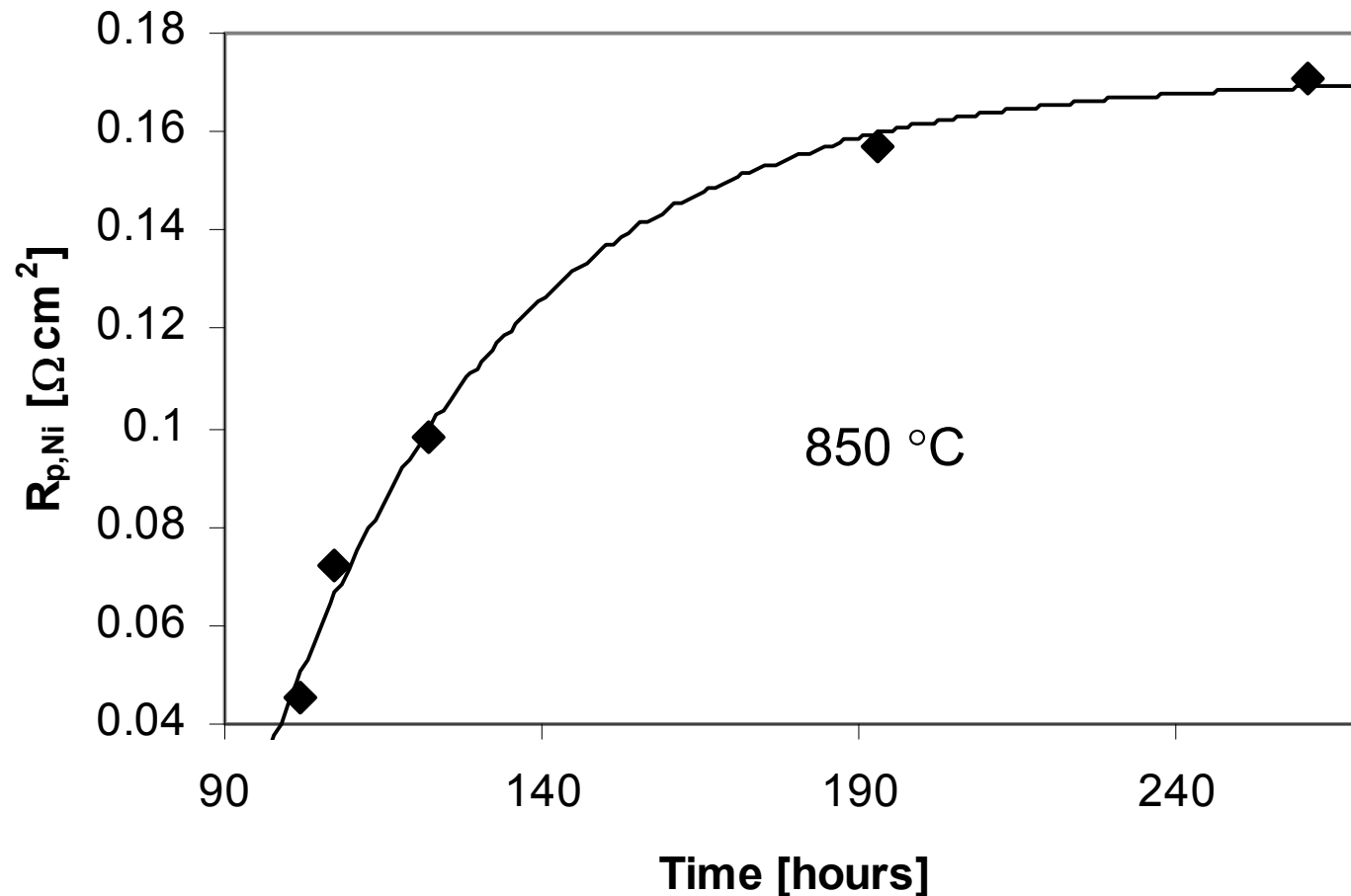


Pure O₂ at the cathode - thus anode investigation

From: Hauch & Mogensen,
SSI 181 (2010) 745–753

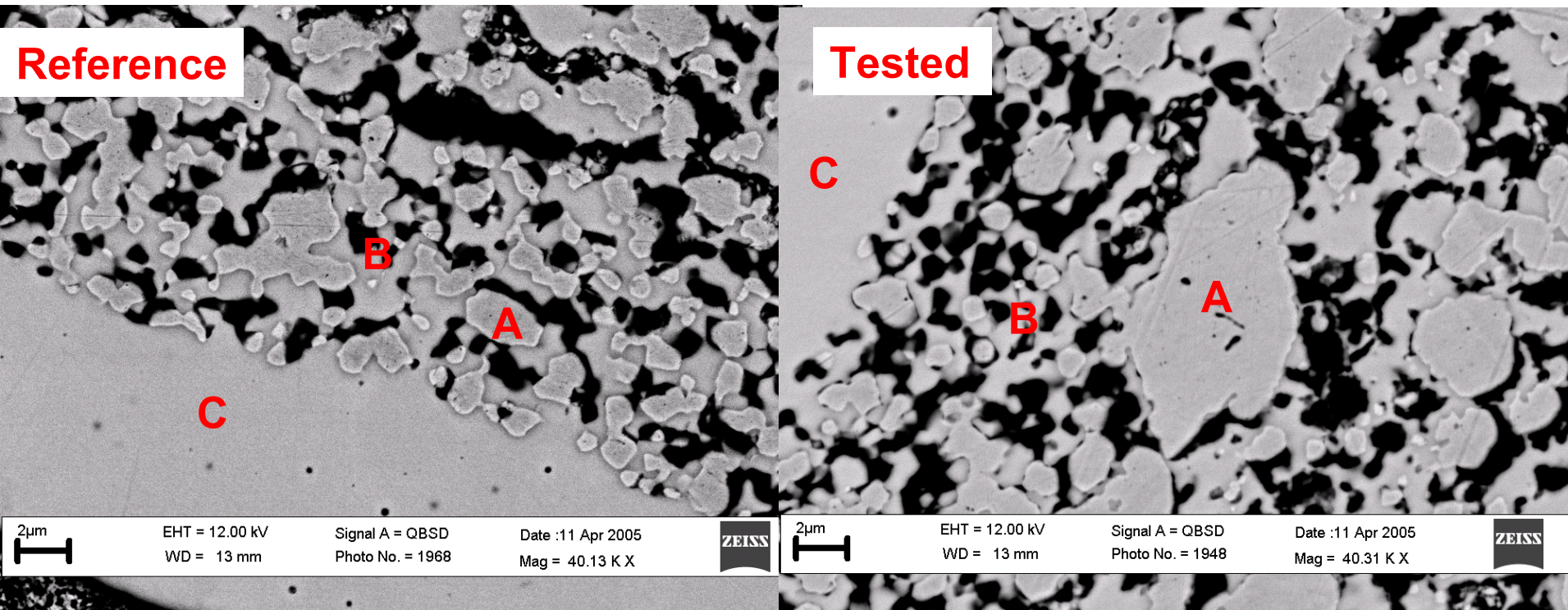
Cell voltage vs time at 750 °C and 0.75 A/cm² for test A: “reference” test; test B: H₂ gas cleaning applied; test D: after 440 h at OCV and (H₂O)/p(H₂)=0.4/0.6, without H₂ gas cleaning; and test E after 332 h of OCV testing at p(H₂O)/p(H₂)=0.4/0.6 H₂ and H₂ gas cleaning.

Ni-YSZ electrode degradation at high pH₂O



Increase in $R_{p,Ni}$ as a function of time at OCV as measured by EIS in 98% H₂O and 2% H₂. The fit of the type $(1-\exp(-t/\tau))$ shown gives a time constant, τ , of 38 hours

Ni-YSZ electrode degradation - high pH_2O 98% H_2O and 2% H_2



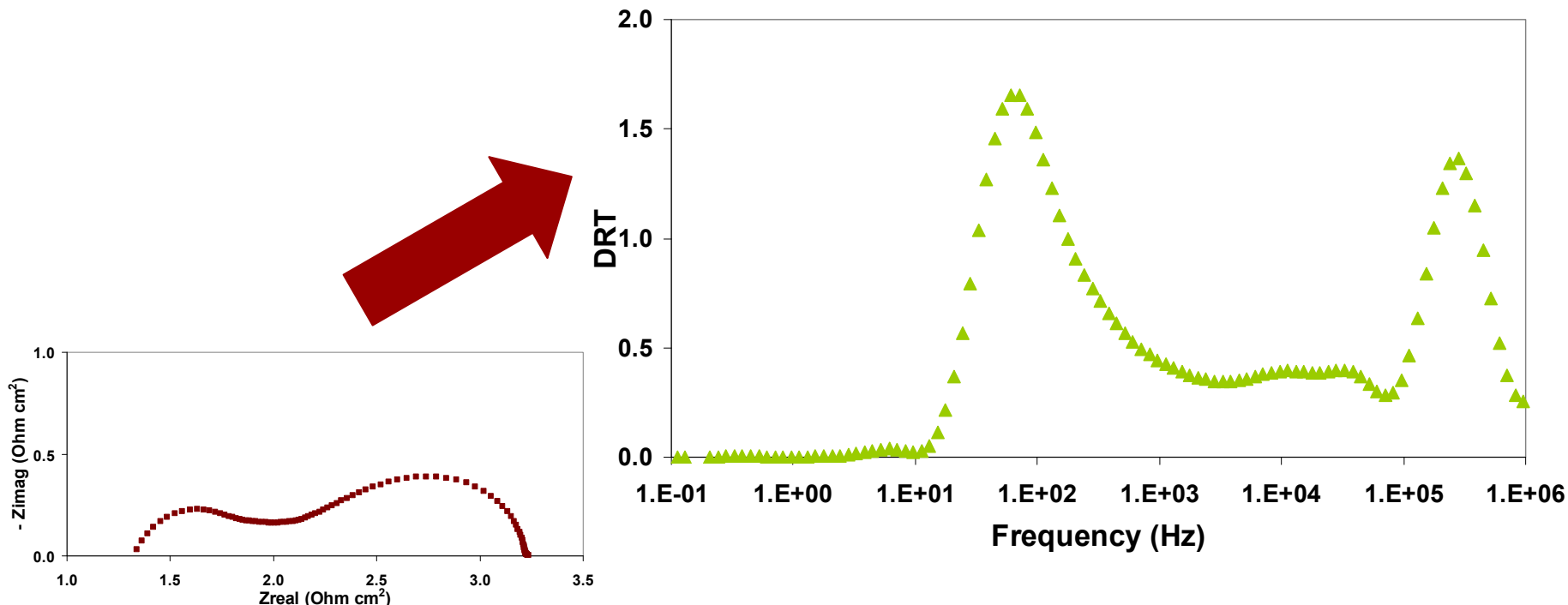
SEM images of the YSZ-Ni/YSZ interface. Reference cell (left) and tested cell (right). A: Ni particle, B: YSZ in electrode, and C: YSZ electrolyte.

More EIS - DRT and ADIS to come

Any questions now?

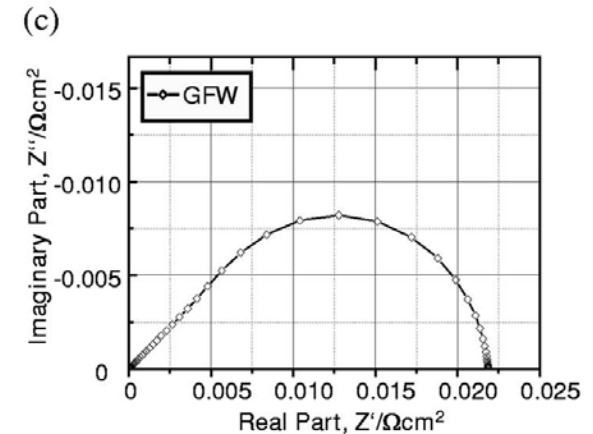
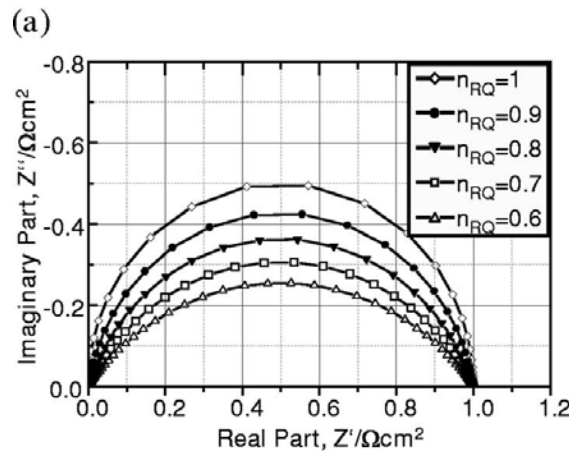
Distribution of relaxation times (DRT)

- Distribution of relaxation times is gained by a Fourier transform of the impedance data, giving a clearer picture of the number of physical processes and their nature

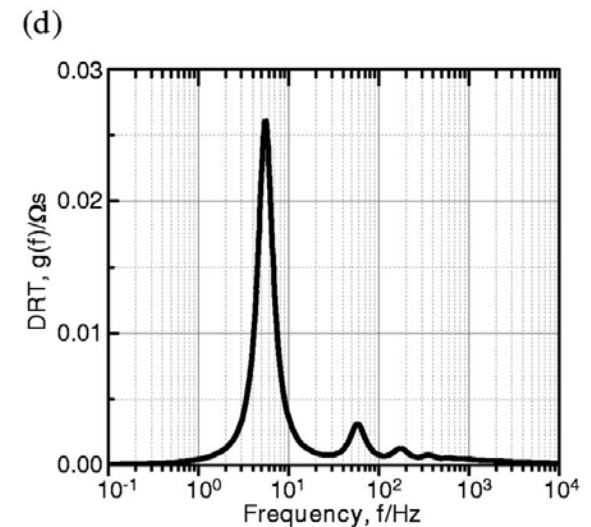
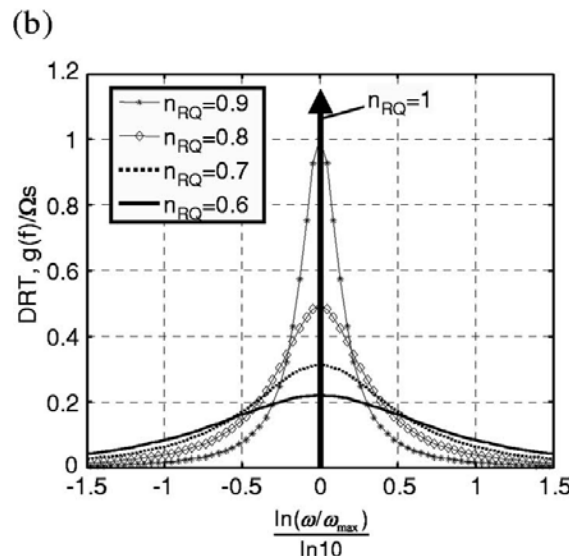


Distribution of relaxation times (DRT)

Nyquist representation

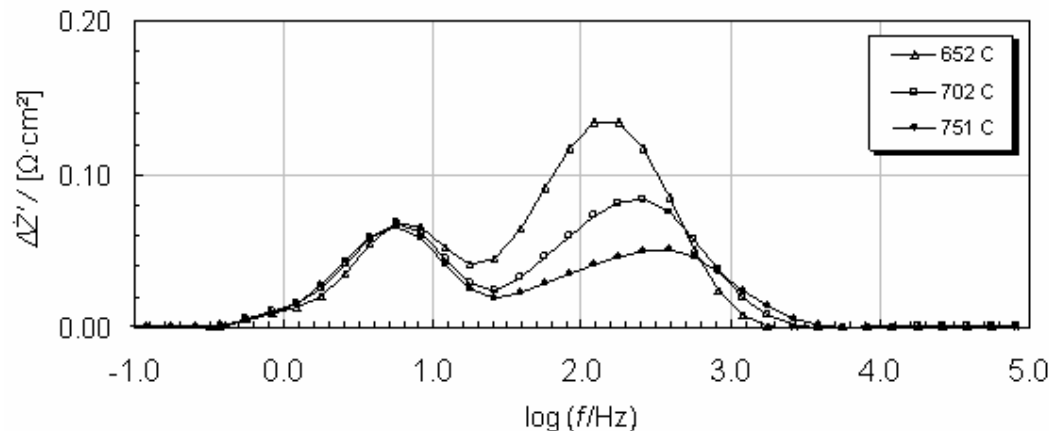
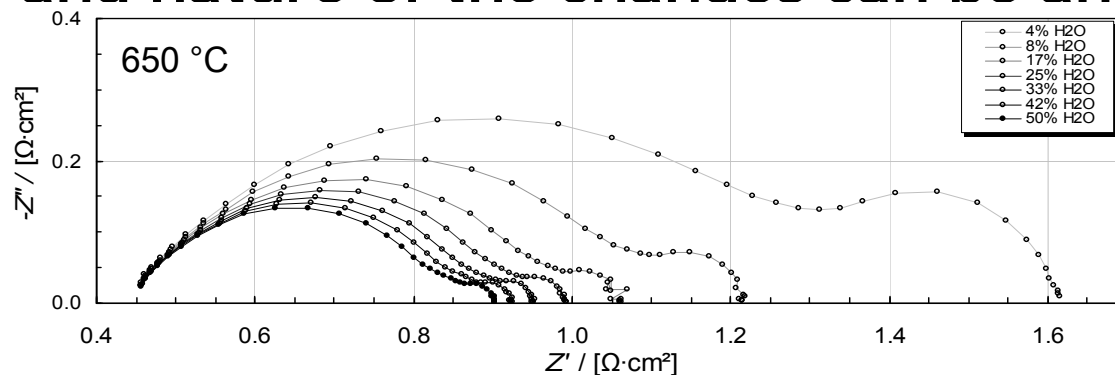


DRT representation



Analysis of differences in impedance spectra (ADIS)

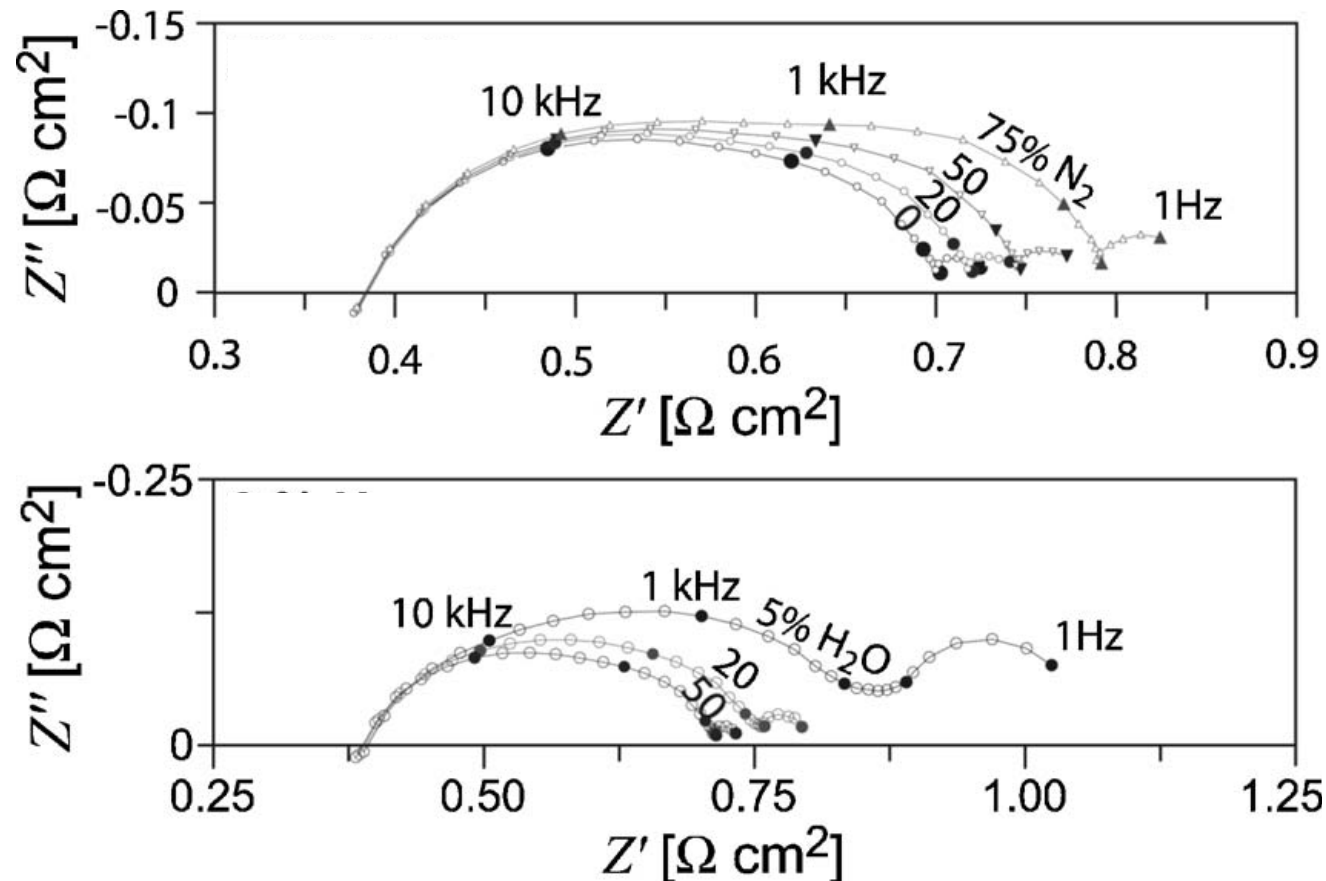
- An impedance spectrum often changes when the temperature or gas composition is changed. When analysing the differences between spectra, the number and nature of the changes can be analysed



Jensen et al. 2007, J. Electrochem. Soc. 154 B1325

Hjelm et al. 2008, ECS Transactions 13 285

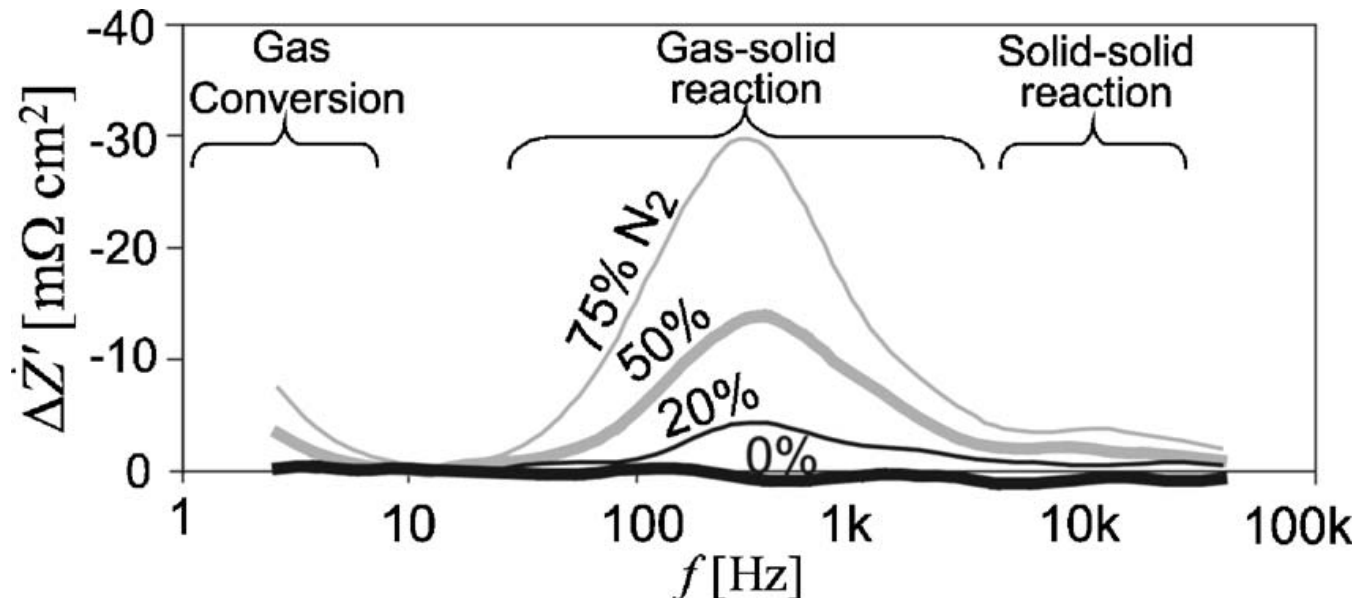
Analysis of differences in impedance spectra, ADIS



Top: EIS - O_2 diluted with 0, 20, 50, or 75 vol % N_2 to LSM/YSZ, 50 % H_2 -50 vol % H_2O to Ni/YSZ. Bottom: EIS - H_2 with 5, 20, or 50 vol % H_2O to Ni/SZ electrode and pure O_2 to LSM/YSZ.

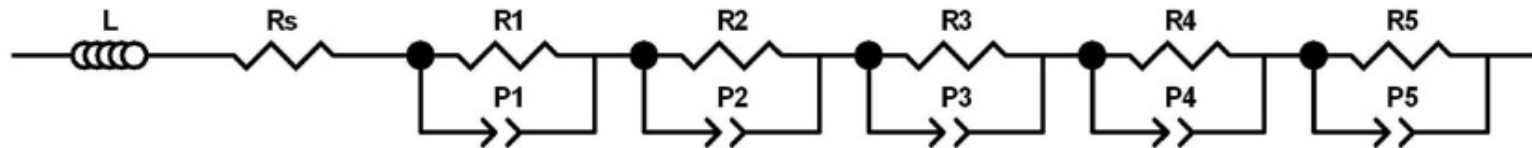
ADIS cont.

Højgaard et al., *J. Electrochemical Society*, **154** (2007) B1325



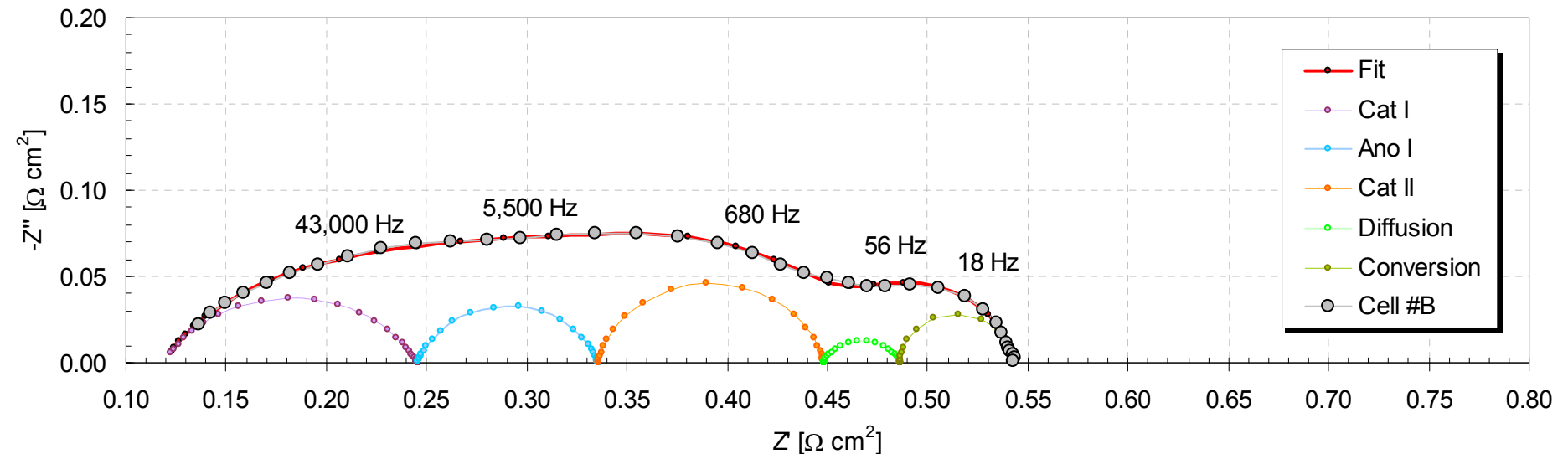
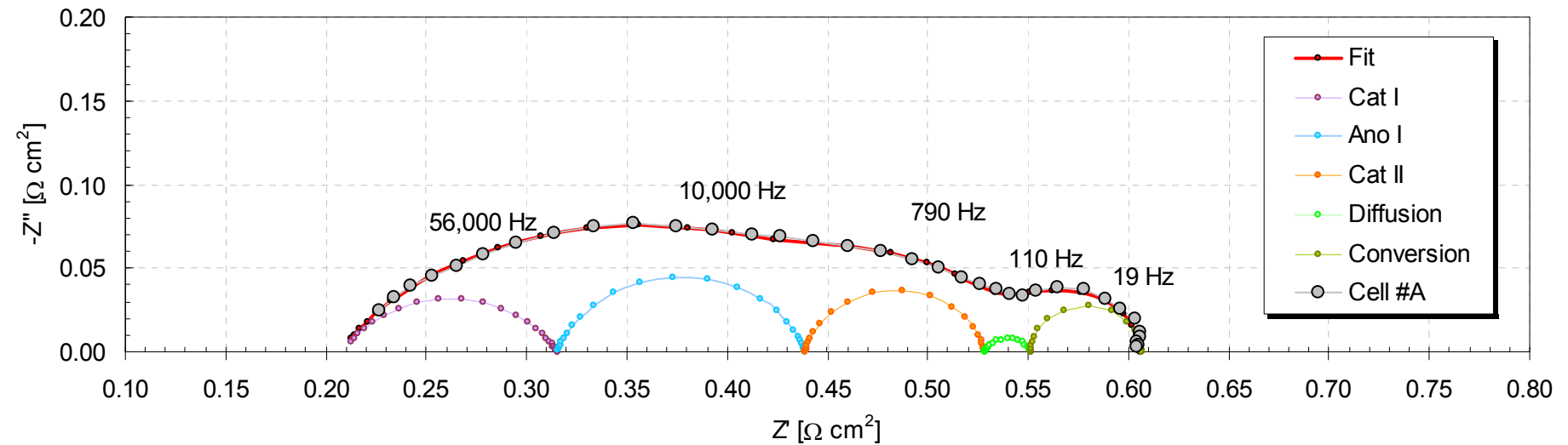
$\Delta Z'$ spectra for gas shift to the LSM/YSZ electrode from pure O_2 to O_2 diluted in 0, 20, 50, or 75 vol. % N_2 . The bold line 0% is a background noise measurement. 50/50 % $\text{H}_2/\text{H}_2\text{O}$ to the Ni/YSZ.

Equivalent circuit model

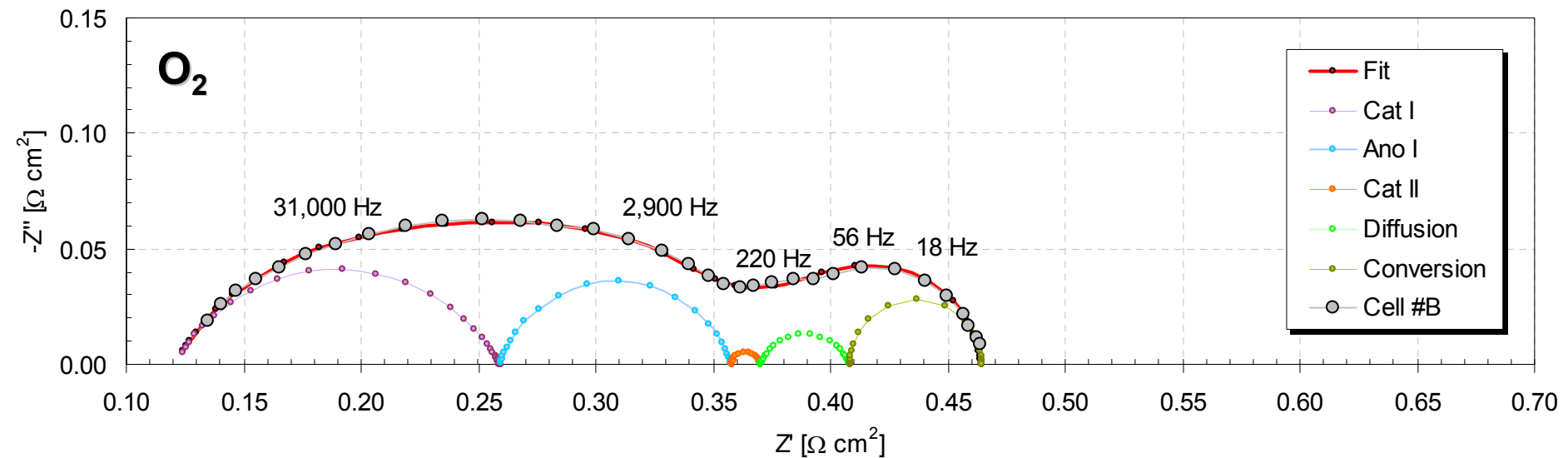
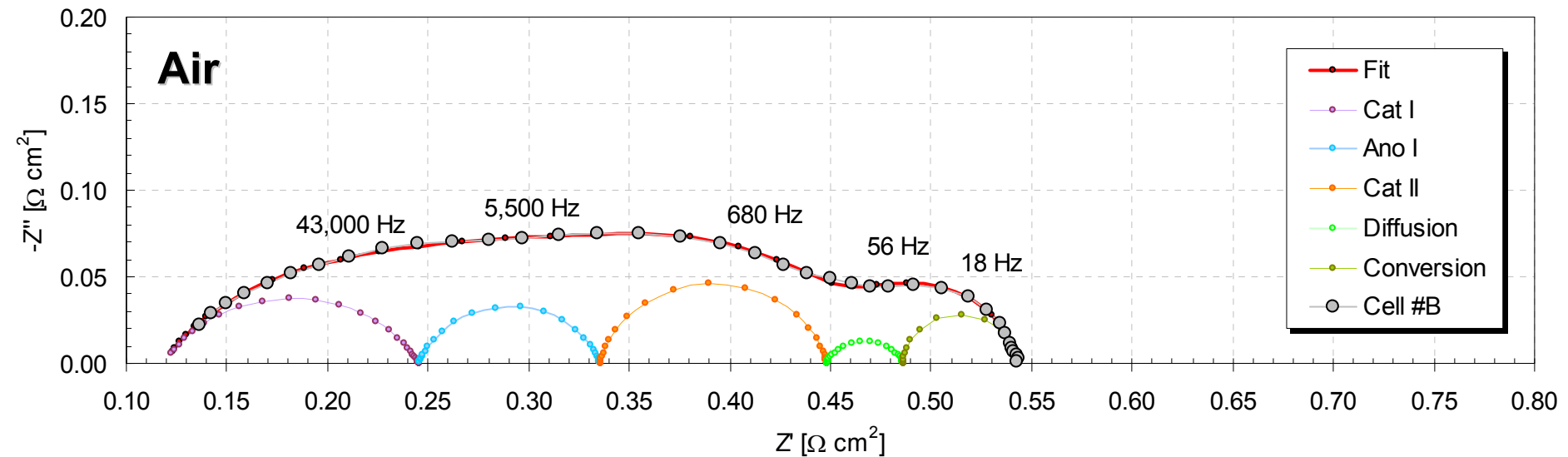


Having data from symmetric cells for both the SOFC anode and cathode plus ADIS + DRT then an equivalent circuit may be established (see e.g. Barfod et al., FUEL CELLS, 06 (2006) No. 2, 141) that can model the cell behaviour relatively precise.

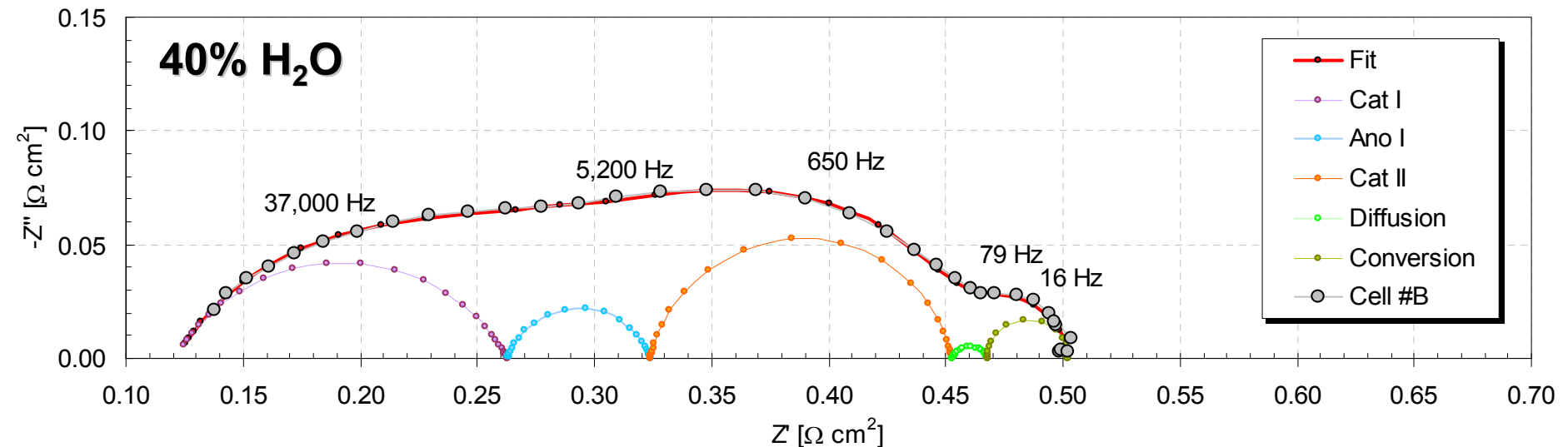
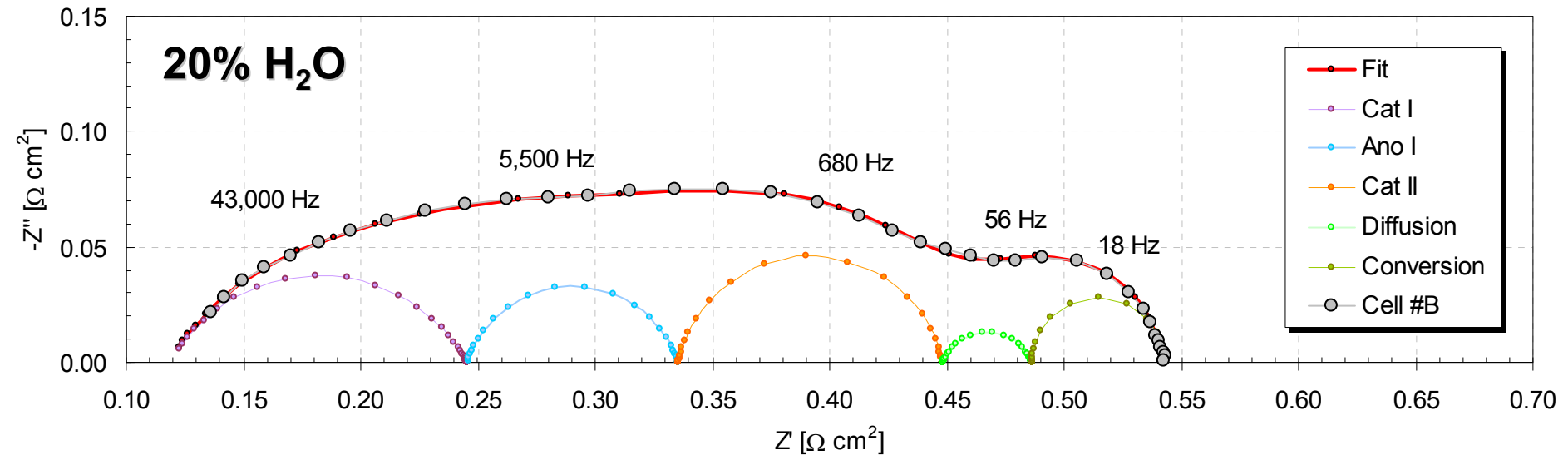
Electrochemical model validation: 750°C, 20% H₂O, air



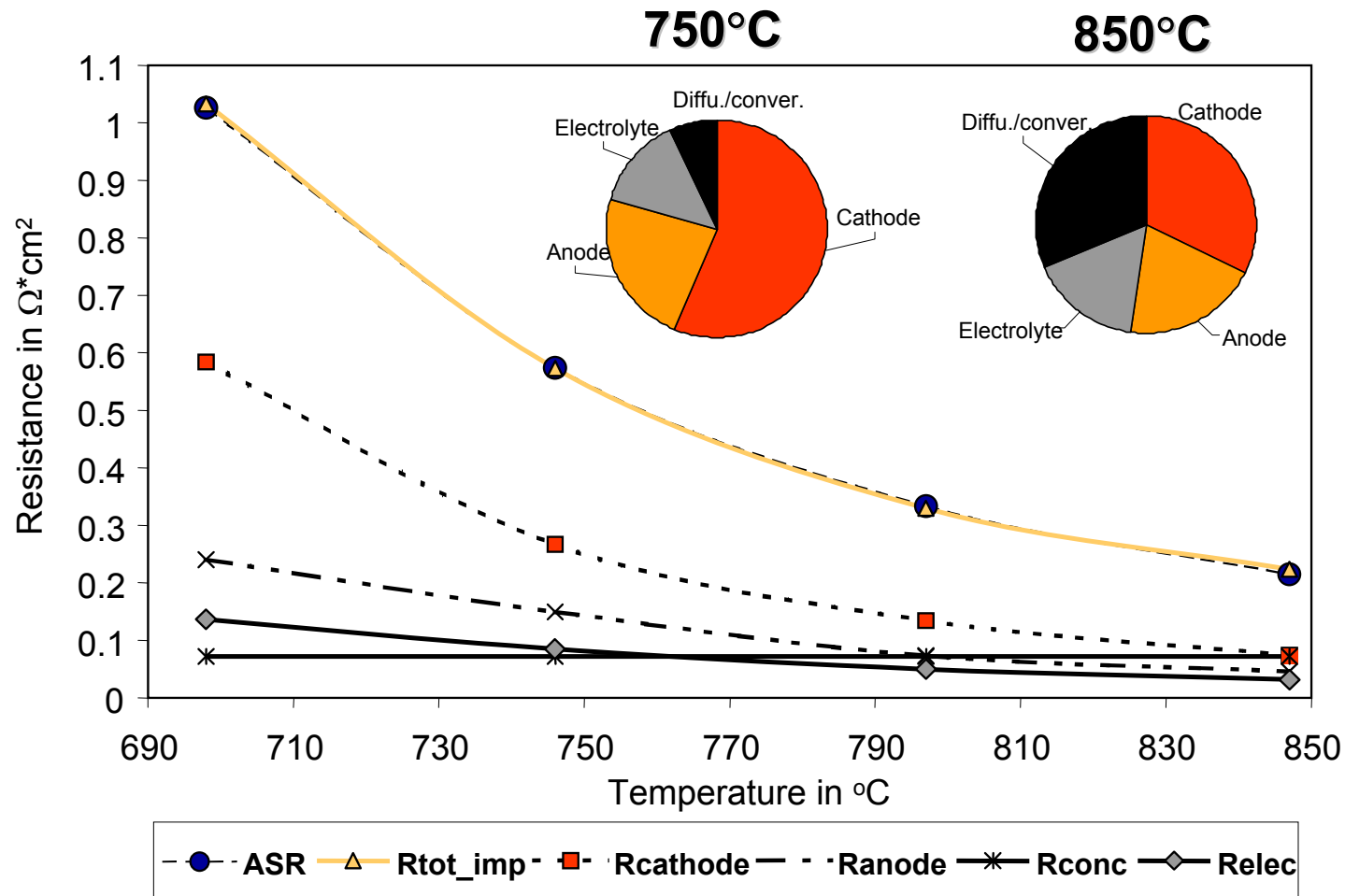
Cell B, 750°C, pO_2 variations, 20% H_2O anode



Cell B, 750°C, pH₂O variations, air cathode



Break down of losses for Risø 2G Ni-YSZ/YSZ/LSM-YSZ cells



Prevention of degradation

- Do not load the cell too hard - find the allowable current density for your cathode
- Do not go to fuel utilisation (high steam partial pressure) above ca. 90 %. Again test the limit for your cell.
- Take care of removing or scavenging (e.g. $\text{CrO}_2(\text{OH})_2$ - H_2S) potential poisons in the feed gases and in the raw materials.
- Make stable electrode structures of stable materials - this is however a long story, which, hopefully, my colleagues teachers have informed you about.

Literature:

Mogensen, Hendriksen, *"Testing of Electrodes, Cells and Short Stacks"*, Chapter 10 in *High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*, Eds. Singhal and Kendall, pp. 261 -290, Elsevier 2003.

Thank you for your attention